EFFECT OF COAL STRUCTURE ON SPONTANEOUS HEATING USING FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF TECHNOLOGY
IN
MINING ENGINEERING

BY

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ROURKELA – 769008

(2013-2014)

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UNDER THE SUPERVISION OF

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CERTIFICATE

This is to certify that the thesis entitled **Effect of Coal Structure on Spontaneous heating using Fourier Transform infra-red Spectroscopy** being submitted by Kanhaia Kumar (Roll No. 110MN0567) to National Institute of Technology, Rourkela; for the award of degree of Bachelor of Technology in Mining Engineering is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter substantiated in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

Prof. D S Nimaje
Assistant Professor

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ABSTRACT

The auto oxidation of coal ultimately results in spontaneous combustion which is the major cause for mine fire in coal mines. It has been a major cause of concern in coal producing countries like India, Australia and China. Therefore the assessment for this auto-oxidation is necessary. It depends upon the different characteristics as well as properties of coal. Once the combustion of coal has been initiated, it is very difficult to control that consequently disturbs the environment of mine and it's near-by areas. The spontaneous heating liability of various coals differs over a wide range and it is required to assess their degree of proneness for taking preventive measures against the occurrence of mine fires to avoid loss of lives and property, sterilization of coal reserves, environmental pollution and concerns about safety and economic aspects of mining etc.

This B.Tech. dissertation deals with the effect of faliphaticity of coal with respect to spontaneous combustion and the relation of proximate analysis and calorific value of coal with the faliphaticity using FT-IR Spectroscopy (Fourier Transform Infra-red Spectroscopy) of some Indian coal. Twenty in-situ coal samples for the project were collected from different coalfields of India like BCCL, CCL, MCL, NEC, SECL, and SCCL, both from opencast as well as underground projects.

The intrinsic properties of the coal samples were determined by following experimental techniques:

- Proximate analysis
- Gross Calorific Value
- Fourier Transform Infrared Spectroscopy(FT-IR)

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CHAPTER – 1

INTRODUCTION

1.1 BACKGROUND

Coal is source of around 27% of world‘s energy consumption and it counts for about 34% of electricity generated across the world. Coal is also a dominant source of energy in India and meets 55% of country‘s primary commercial energy production. Mine fires in Indian coalfields is generally due to spontaneous heating of coal irrespective of various preventive technologies being adopted. The spontaneous heating of coal varies over a wide scale and it is required to assess their degree of proneness for taking necessary preventive measures against the occurrence of fires that leads to loss of lives and property, sterilization of coal reserves and environmental pollution and concerns about safety as well as economic aspects of mining[20].

In order to find out the liability of coal towards spontaneous heating different methods have been adopted by various researchers of the world. Various experiments have been carried out for assessing the spontaneous heating liability of coal viz., Crossing point temperature, Wet oxidation potential, Differential thermal analysis, Flammability temperature. This propensity to self-combustion of coal is an important parameter in determining the incubation period of coal seam, which decide the size of pillars to be formed and the rate of extraction, which is an important safety measure in mine planning. It is therefore important for the planners of a mining project to determine in advance the spontaneous heating liability of coal seam/seams to be extracted so that either the coal has been mined before the completion of incubation period, or precautionary measures are taken to tackle this menace. The experimental techniques used to assess the tendencies of coals towards spontaneous heating in the present study are: Proximate analysis, Calorific value determination and the structure off coal using Fourier Transform Infra-red Spectroscopy (FI-IR) [25].

1.2 GENERAL

Coal has been a fruitful resource for ages. It is primarily burned for the production of heat and/or electricity, processing and production of chemicals and also for industrial purposes, such as refining of metals. At least 40% of the world's electricity comes by burning of coal, and in 2012, about one-third of the United States' electrical energy came from coal that is around 49% in the

year 2008. It is the largest source of energy for the generation of electricity across the world. India has some of the largest coal reserves across the world (approx.267 billion tones). The derived energy from coal in India is twice that of energy derived from oil, whereas worldwide; energy derived from coal is about 30% less than energy generated from oil. The top coal producing states in India are Jharkhand, Orissa, Chhattisgarh, West Bengal, Andhra Pradesh and Madhya Pradesh. The World coal consumption in the year 2010 was about 7.25 billion tones (7.99 billion short tons) and is expected to shoot up by 48% to 9.05 billion tones (9.98 billion short tons) by 2030. The coal production of China in the year 2011 was 3.47 billion tones (3.83 billion short tons), while India produced about 578 million tons (637.1 million short tons). 68.7% of China's electricity is generated from coal. The consumption of coal in USA is around 13% of world total in, i.e. 951 million tons (1.05 billion short tons), using 93% of it for generation of electricity. 46% of total power generated in the USA was derived from coal [8].

As per estimation, the proven reserves of coal across the world is beyond 861 billion tons. This means that at the current rate of production the coal would to last us around 112 years. Coal reserves are available in each and every country worldwide, having recoverable reserves in around 70 countries. The biggest reserves are found in USA, China and India [8].

Coal mine fire is a major concern for the coal mining industry across the world. Mine fires can be distinguished into near-surface fires, where the fire extend to the surface and the necessary oxygen for ignition comes from the atmosphere, and deep underground mines, where the oxygen comes through ventilation. Some fires along coal seams are due to natural occurrences. Some coals may self-ignite at very low temperatures as 40 °C (104 °F) for brown coal in the right conditions of moisture and grain size. The fire usually ignites at a few decimeters inside the coal at a depth in which the permeability of the coal allows the inflow of air but ventilation is insufficient to remove the heat which is generated. Thousands of inextinguishable mines are burning across the world, especially in China. Incidents of spontaneous combustion are also preventing in open cast collieries and its stockpiles dicers dumps, train trucks and ships [9].

Spontaneous combustion occurs by self-heating of coal, followed by thermal runway (self-heating which rapidly accelerates to high temperatures) and finally, ignition. When coal is exposed to air, its exposed parts absorb free oxygen at a faster rate than others and oxidation results in the

evolution of several gases such as carbon monoxide, carbon dioxide, etc., water vapour, some heat. This takes place at ambient temperatures that leads to open mine fires [10].

Coal mine fire generates various problems in mines such as damage of machinery, loss of life and property, various health hazards, environmental pollution, roof fall, damage to the support systems and roadways such as haulage systems etc. Coal mine fire is a function of the quality of the coal and the conditions to which it is subjected. The first coal mine fire was reported in Raniganj Coalfields in 1865. A greater extent of mine fires have been reported from Raniganj and Jharia coal fields that have superior non-cocking coal. In 2010, 68 coal mines were under mine fire, burning beneath a 58-square-mile (150 km^2) region of the Jharia coalfield in Dhanbad, Jharkhand. Jharia coalfields has been prone to mine fires. These fires continue to spread along the adjoining areas results in rapid destruction of only source of prime coking coal in the country. To suggest some preventive measures against these mine fires, many researches were conducted to understand the mechanism of spontaneous combustion of coal and run the process of coal production without any interruption that results in saving life, property and environment. A proper assessment of the spontaneous heating susceptibility of coal is done so that mine operators are notified well in advance so that production activities could be planned within the incubation period. Various methods have been adopted by different researchers of the world to find out the susceptibility of coal to spontaneous heating based on the measurement of oxidation rate and ignition temperature such as Crossing point temperature method, Differential thermal analysis, Wet oxidation potential difference method, Differential Scanning Calorimetry Technique, Critical Air Blast and spectroscopy techniques[10].

1.3 OBJECTIVES OF THE PROJECT

The objectives of the project is to find out the faliphaticity of the collected coal samples using FT-IR and the relation with reference to spontaneous heating, the relation of proximate analysis and calorific value of coal with the faliphaticity of coal.

In order to fulfill the above said objectives the following methodology was adopted –

- **Literature review** – Collection of all the past research works done by various academicians/researchers/scientists both national and international.

- **Sample collection and preparation** – Twenty samples were collected from BCCL, CCL MCL, NEC, SCCL and SECL, for the purpose of analysis and the samples were collected and prepared as per the Indian Standards.
- **Experimentation** – the experimentation part divided into three stages:
    1. Determination of intrinsic properties of coal – proximate analysis.
    2. Determination of Calorific value of coal sample – Digital Bomb Calorimeter.
    3. Determine the structure of coal sample – Fourier Transform Infrared Spectroscopy.
- **Analysis** – Analysis of coal structure and determination of Faliphaticity.

CHAPTER – 2

LITERATURE REVIEW

2.1 COAL MINE FIRES

Mine fires are mostly associated with coal mines, though fire in pyrite mines and occasional fire due to timber in certain metal mines are also observed. Mine fires occur frequently in coal mines but are rare in metal mines. The possible reasons of mine fire are spontaneous heating, blasting, explosion of gases, electrical failures. In coal mines the major cause of mine fire is auto oxidation of coal. Coal mine fires may start either from open fires over the external agencies or originate due to very nature of coal. The property of coal to liberate heat when it comes in contact with oxygen and its poor thermal conductivity favors heat accumulation that may extend to coal mine fires. The former type of fire from external agencies is known as Exogenous Fires and the latter type i.e. due to self-heating characteristics of coal is called Endogenous Fires or Spontaneous Combustion [22].

Endogenous fires [22]

1. Pyrite fires: Pyrite (FeS_2) is a polysulphide of iron containing 46.37% Fe and 53.33% S. When pyrite reacts with oxygen present in atmosphere an exothermic reaction takes place leading to liberation of heat, giving rise to spontaneous heating. Spontaneous heating liability of pyrites is much less than that of coal but it increases with increase in carbonaceous materials present in pyrites. Incidents were observed when pyrites with 5 - 6 %Carbon and 10 – 12% Sulphur have caught fire due to spontaneous heating (Amjhore, India).

2. Endogenous heating timber: Decayed timber offers extremely favorable conditions for spontaneous heating, mainly due to bacterial formation

Exogenous fires [22]

Current electricity is one of the prime causes of mine fires. It may originate from short circuiting, electric bulbs, over heating of machines, candles, flames from fires or explosion while blasting and ignition of inflammable materials like timber, oil and wastes. At times crushing of sulphide ores or surface fires may also be the origin.

2.2 HISTORY OF COAL MINE FIRES IN INDIA

First incident of mine fire reported in the year 1865 over the mines of Raniganj coalfields. Various occurrences of mine fires have been reported over 140 years from Jharia and Raniganj

coal fields. Mine fires not only endangers the lives of men but also cause considerable economic loss to the company and subsequently the loss of mineral for the country. These fires continue to spread along adjoining areas and also restrict the economic exploitation of coal seam present in vicinity or contiguous seams. The other major effects of mine fires include environmental pollution by emission of huge quantities of steam, smoke and noxious gases posing serious health concerns. In Indian coal mines 75% of the coal fires occur due to spontaneous combustion. Most of the coal seams in India are thicker as compared to the rest of the world and there is a tendency of spontaneous heating during depillaring operation in bord and pillar method of extraction. Extraction of thick seams and standing coal pillars are always difficult especially if they if the coal have high moisture content, high volatile content and low ash content are more liable to spontaneous combustion. It is not practicable to extract all the coal by caving method or even by complete packing under Indian mining condition. Pillars standing for long time are liable to deteriorate in straight and spilling may occur.

Fig 2.1 Coal Reserves of India [18]

2.3 SPONTANEOUS HEATING OF COAL [2]

It is a phenomenon in which the coal catches fire automatically when comes in contact with oxygen present in the atmosphere without any external source of fire which leads to mine fires is known as spontaneous heating of coal. The prime cause of spontaneous heating is the self-oxidation of coal. Although the actual mechanism of coal oxidation is yet unknown, there are many theories put forward for explanation of the coal oxidation and combustion.

2.4 MECHANISM OF SPONTANEOUS HEATING [2]

The auto oxidation of coal is a complex physico-chemical process comprising a series of events like absorption of oxygen, complex formation of coal-oxygen and their decomposition leading to the discharge of heat. Complexity of this process is vast because of the greater diversity of coal with associated mineral matter and prevailing conditions during oxidation.

During the oxidation of the heterogeneous mass, various concurrent and overlapping reactions takes place which are difficult to separate out. The rate of oxidation at ambient temperatures gives a measure of the proneness of coal to spontaneous heating. This low temperature aerial oxidation of coal is not a singular chemical process but a complex phenomenon generally comprising of several simultaneous and interesting chemical processes which result both in erosive material removal and structural alteration of the organic matter. A large number of stable chemical chain reactions take place due to several oxidation states of carbon and a variety of strong carbon oxygen complex is formed. The noticeable compositional, elemental and structural variations reveal that the reaction of oxygen with solid coal is a time dependent dynamic method. Noticeable variations in coal molecular structure and composition arise from prolonged sequence of events whose components exhibits complex inter-relationships. Thus the reaction environment is heterogeneous intrinsically because two bulk phases, solid and gas are present and extrinsically because various structural changes brought by the reaction, affect the overall coal reactivity. Porous solid absorbs the liquids or gases or the solution of gas/liquid, which is known as sorption. When accumulation restricts at the surface liberating heat and rate of penetration is negligible then it is considered as adsorption but if uniform penetration in the bulk of the solid occurs, then it is called absorption. The absorptions is always an endothermic phenomenon and starts from the surface of the solid and consumes heat of the solid for penetration. The energy on the surface is always low. The method where physical forces like inter-molecular attraction are blamable, are known as physical

adsorption or Van der Wall's adsorption, but when operative force needs to break the chemical nature of the compound is called chemisorption or activated adsorption. This physical adsorption is predominant at very low temp whereas chemical adsorption is very low at low temp whereas rate of reaction increases with increase in temperature. Coal gets heated up on absorbing oxygen, whose decomposition phenomenon can be expressed/explained in the following manner. Oxidation is very slow below 50^0 C and accelerates above 50^0 C, but above 80^0 C, a period of steady state is maintained, probably due to the removal of moisture of coal. The removal of oxides of carbon occurs from 120^0 C. The interaction of oxygen with coal accelerates rapidly up to 180^0 C and thermal decomposition starts between 180^0 C to 220^0 C. Self-sustained process of combustion begins in between 220^0 C to 275^0 C with very rapid rise of temperature until the ignition point is attained [2].

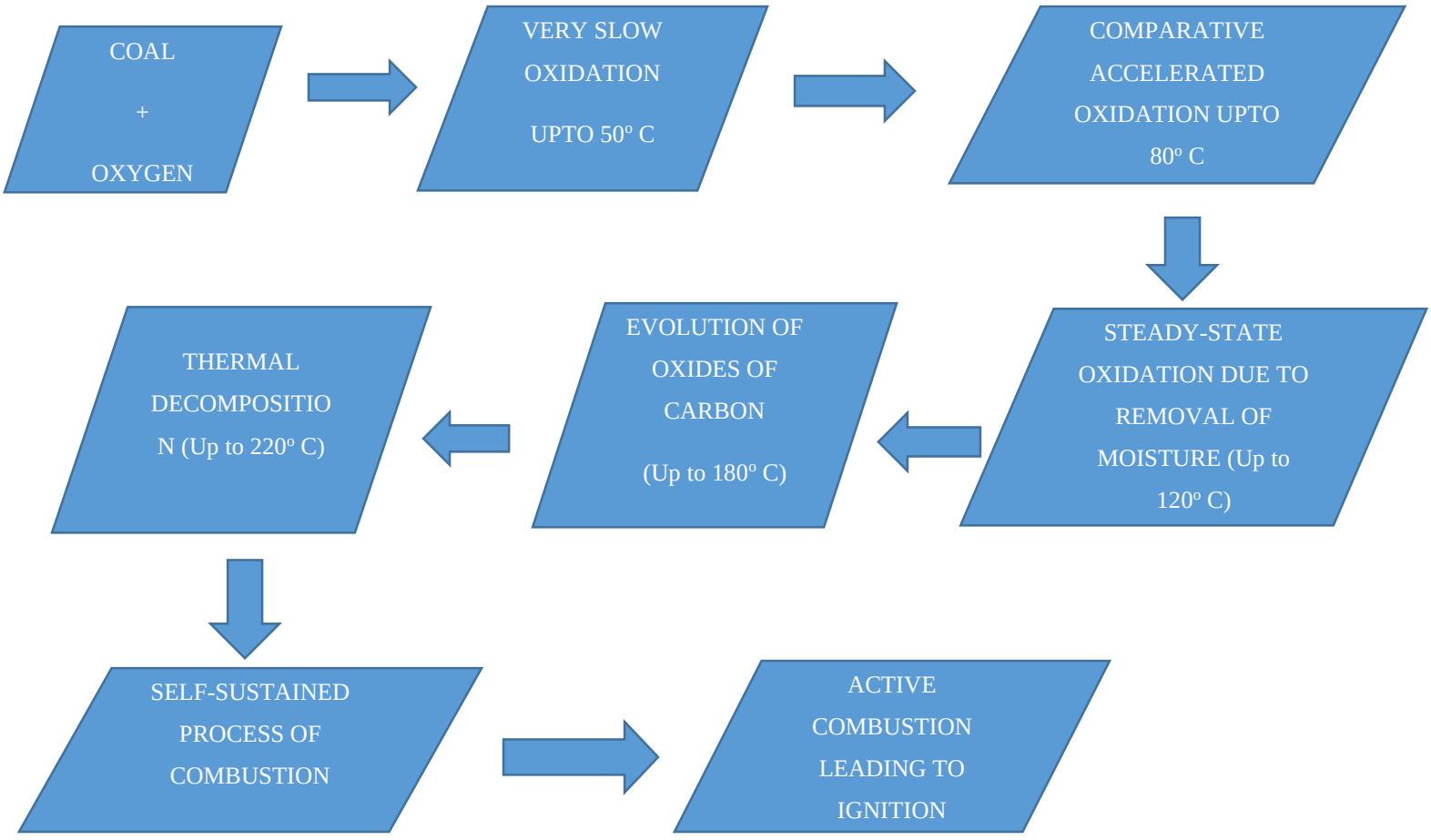


Fig 2.2 Sequential Stages in Spontaneous Combustion of Coal [2]

2.5 THEORIES OF SPONTANEOUS HEATING [2]

2.5.1 Coal Oxidation Theory

The overall oxidation process of coal depends on the following factors:

- Temperature – Under normal conditions the rate of chemical reaction increases with rise in temperature and is almost doubled for 10° C rise in temperature. The minimum temperature required for reaction between coal and oxygen is 80°C during which it is physical adsorption and chemisorption at room temperatures.
- Type of coal – The mechanism of oxidation is same for every type of coal but the availability of active centers define the proneness of coal towards spontaneous heating. Usually low rank and high moisture coal have higher oxygen affinity with better ease of peroxy-complex formation and hence greater tendency towards spontaneous heating.
- Extent of oxidation – as the time of exposure of coal surface to atmosphere increases the rate of oxidation reaction gradually decreases and coal gets weathered. In the initial stages, the macro pores present on the surface determines the oxygen consumption whereas in later stages the micro pores determine.
- Moisture – As moisture content of coal increases the heat required for spontaneous combustion increases by heat of wetting released. It helps in the formation of peroxy complex and influences the rate of reaction. Release of moisture from coal produces more active centers making it more liable to spontaneous heating.

2.5.2 Pyrite theory –

- Pyrites are present as impurities in coal and acts as major sources of heat. The oxidation of pyrites is given by the following reaction:

$$2\ FeS_2 + 7\ O_2 + 16\ H_2O = 2\ H_2SO_4 + 2\ FeSO_4.7\ H_2O + 316kcal$$

The reaction of pyrite with oxygen in presence of water is an exothermic reaction that produces heat which is capable of triggering combustion of coal. The products formed after the reaction have greater amount of volume as compared to pyrite and hence break open to the surface they are embedded in. But it has been observed that pyrites can be the cause of spontaneous heating if they are present in considerable proportions.

2.5.3 Bacterial theory –

Spontaneous heating observed in woods and haystacks are mainly due to bacterial action. Different evidences showed that specific bacteria's have the capability to grow over coal and in some cases they caused a slight rise in temperature of the coal. Graham observed that sterilized coal oxidized at the same rate as the unsterilized coal and concluded that mechanism of oxidation did not include bacterial activity. Fuchs however concluded that bacteria could cause only a slight heating which may not play any significant role.

2.6 FACTORS AFFECTING SPONTANEOUS HEATING [4]

The primary reasons for difficulty in understanding the mechanism of spontaneous combustion is the presence of many internal and external factors affecting the initiation and development of the phenomenon. These factors have been reviewed by various researchers.

The main factors which have significant effects on the process are summarized below:

2.6.1 Intrinsic factors – These factors are mainly related to nature of coal

- Pyrites – As the pyrite content increases the tendency of coal towards spontaneous heating also increases.
- Inherent moisture – Changes in moisture content such as drying or wetting of coal have significant effects.
- Particle size and surface area – As particle size increases the exposed surface area decreases and the susceptibility decreases.
- Rank and Petrographic constituents – Lower rank coals having less value of gross calorific value are more susceptible to spontaneous heating.
- Chemical constituents – Ash generally decreases liability for spontaneous heating but certain parts of ash such as lime, soda; iron compounds have accelerating effect whereas alumina and silica have retarding effects.
- Mineral matter – Some chemicals promote an others inhibit spontaneous heating.

2.6.2 Extrinsic factors – These factors are mainly related to atmospheric, mining and geological conditions

- Extraneous moisture – Evaporation of surface moisture leads to release of heat of wetting which adds to the temperature rise and increases susceptibility. Presence of atmospheric moisture increases rate of oxidation of coal.
- Temperature – Higher surrounding temperature leads to increase in oxidation process and ultimately in spontaneous heating of coal.
- Method of working, ventilation and air flow rate – Mining methods such as bord and pillar mining that leave some pillars attracts more spontaneous heating than longwall methods. Air flow rate controls heating to a large extent. If the ideal flow rate is maintained then it helps in dissipation of heat but if too much of air is flowing then it stagnates the heat and increases the heating.
- Oxygen concentration – Higher the oxygen concentration in the atmosphere more rapid is the oxidation process as oxygen is readily available.
- Coal seam and surrounding strata – Presence of faults that lead to the passage of air and oxygen to the heating are generally increase the rate of heating.
- Timbering, roadways, bacteria and barometric pressure – Presence of timbers in the mines leads to the danger of catching of fire which gives the heat required for spontaneous heating of coal. Bacterial decomposition of coal and other wood products also releases some amount of heat which increases susceptibility.

2.7 NATIONAL AND INTERNATIONAL STATUS

Several research work and studies has been carried out across the world by various researchers to assess the spontaneous heating liability of coal. Some of the researches has been summarized below:

- **Ndaji (1995)** reported FT-IR study of oxidation of coal samples. They reported that the ratio of aliphatic to aromatic content of different coals varies from 3.33 to 0.91 and these aliphatic components decreases at different rates for different components i.e. the rate of decrease of aliphatic components with temperature differs from one coal to other, however the oxidation of coal even at low temperatures below 200^0 C, reduced the aliphatic/aromatic ratio and increases the hydroxyl/aromatic ratio along with an increase

in oxygen containing functional groups like C=O, -COOH, etc. All these confirm the process of oxidation of hydrocarbons in coal with an increase in temperature leading to loss of aliphatic moiety from the coal structure through thermal and catalytic fragmentation leading to increase in the aromatic nature of the coal content.

- **Cetinkaya (1998)** observed the decrease in the peaks of aliphatic C-H due to oxidation leading to increase in C=O peaks in the coal samples. But as the temperature reaches around 250^{o} C, C=O peaks shows decreasing trend with further increase in temperature and as the temperature consequently reaches 500-550^{0} C, peaks almost disappeared.
- **Huai et al. (1994)** inferred that the increasing maturity of coal can be directly related to the increasing geothermal gradient that the coal have been subjected to and is accompanied by the expected increase in aromaticity and subsequently related to increase in the atomic structure.
- **Rao et al. (2011)** concluded that with increase in Faliphaticity of a coal sample, the liability towards spontaneous heating also increases. For a coal sample if Faliphaticity is high and in addition if it decreases at a faster rate with increase in temperature, such a coal is highly prone to spontaneous combustion.
- **Guangheng Wang et al. (2011**) carried out an investigation for the time evolution of the coal structure at low temperature at nearly 120^{0}C for the time period of 14 days. The characterization of the coal sample was done with the help of FT-IR. It was found that the groups like carboxyl and ether group are main feature for increasing the oxidation of the coal. It was found the aromatic structures had also positive effect on the spontaneous oxidation of the coal.
- **Wang Deming et al. (2013)** observed that **i**t was a tough job to select a particular efficient inhibitor to retard the spontaneous combustion of the coal due to the presence of the complex structures. The analysis of the complex coal structure was done with the help of FT-IR (Fourier Transformation Infrared spectrum). Elucidation of the active functional group was undertaken to develop an effective method for determination of an efficient chemical inhibitor. The justification of the approach was checked using the CPT, oxygen consumption, CO emission rates. The FT-IR analysis was used to monitor the distribution and changing the concentration of active functional groups. The active groups with lower activation energy were eliminated by chemical inhibitor to eradicate the future oxidation.

- **Beamish et al. (2013)** carried out an investigation on few reactive coals from Australia and US were used to enumerate the consequence of the effect of adding the anti-oxidant agent; a moist coal adiabatic oven test was undergone. For the particular dose of the inhibitor applied to the coal sample, there was a substantial reduction in the self-oxidation of the coal. For bituminous coal there was an extension by a factor, while it was double for the highly volatile bituminous coal. The result made out of the experimentation was similar with the site experience on the application of the anti-oxidant on the spontaneous coal.

2.8 FI-IR SPECTROMETER [26]

2.8.1 Construction of instrument

A conventional IR spectrophotometer consists of a sample IR beam that is directed through the sample chamber and measured against a reference beam at each wavelength of the required spectrum. IR spectroscopy has drastically improved by the development of Fourier Transform method.

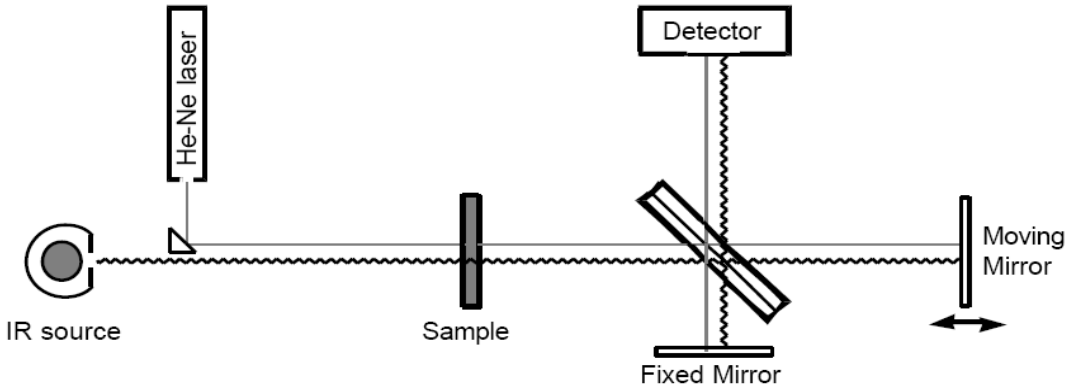


Fig 2.3 Diagram of Michelson interferometer used in FT-IR Spectrometer [26].

In the above experimental set-up, radiation from the inferred source is directed through the sample cell to the beam splitter. The radiation is divided into two equal halves, on half is been reflected from a fixed mirror and the other half is reflected from another mirror which moved continuously over a distance of about 2.5 micrometers. When two beams recombine at the detector, an interference pattern is produced.

2.8.2 Principles of infra-red spectroscopy [26]

Organic molecules absorb IR radiation between 4000cm^{-1} and 400cm^{-1} that corresponds to absorption of energy between 11kcal/mole and 1 kcal/mole. This energy provides the threshold energy required to make transition from ground state to exited state in within the molecule.

IR spectroscopy is a very important tool for the identification of functional groups. The important regions of the IR spectrum are above 1650cm^{-1}, whereas the fingerprint region (600 cm^{-1} to 1500 cm^{-1}) cannot be easily used for verification of unknown functional groups. Transitions between vibrational energy levels follows the classical harmonic oscillator. The interpretation of Infrared spectra depends on the understanding of five basic principles:

1) **K** – The force constant

   K is proportional to bond order or bond strength. For example, C-O vibrates at a lower frequency than C=O. Also, the change in the force constant of different carbonyl groups can be explained based on the contribution of resonance structures. The base value for stretching frequency of a carbonyl (e.g., acetone) is 1715cm^{-1}. Acid chlorides have bond order slightly greater than 2 and phenyl ketones, vinyl ketones and amides have a CO bond order less than 2 because of resonating structures.

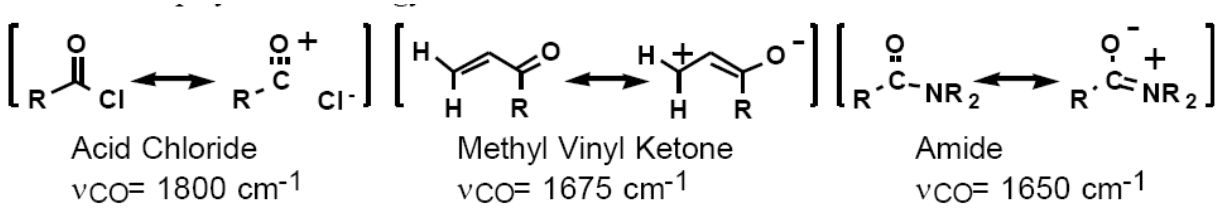


Fig.2.4 Comparison of bond orders of Acid Chloride, Methyl Vinyl Ketone and Amide [26].

2) **μ** - Reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Where m_1 and m_2 represents the atomic mass of concerned molecule. As the atomic mass increases, the molecule becomes heavier that results in slower vibration of molecule. So, as the reduced mass increases the frequency of oscillation decreases.

3) Overtone peaks

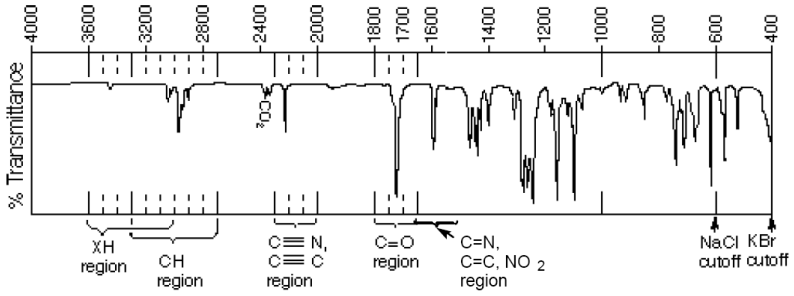


Fig 2.5 Regions of functional groups with important peaks [26]

In the above spectrum a small peak is observed at 3450 cm^{-1}, even though the compound does not have any O-H or C-H bonds.

TABLE 2.1 CHARACTERISTIC OF IR FREQUENCIES [26]

X-H Region (3600cm^{-1} to 2400cm^{-1})

Frequency (cm^{-1})	Content	Comments
3600	υ(free OH)	Sharp peak Alcohol or Phenol free OH
3600-2800	υ(H-bonded OH)	Very Broad peak: Alcohol: 3400 to 3200 cm^{-1} ; Phenol: 3600 to 3000 cm^{-1} ; Carboxylic Acid: 3600 to 2400 cm^{-1}
3500-3300	υ(NH)	Amines show broad peaks, Amides show sharp peaks Primary Amines display two peaks (υ_s and υ_{as})

CH Region (3300 cm^{-1} to 2700 cm^{-1})

Frequency (cm^{-1})	Content	Comments
3300	Alkyne ν(CH)	strong, sharp
3150-3000	Alkene or Phenyl ν (CH)	medium intensity
3050	Cyclopropane or Epoxide ν(CH)	Weak
2960,2870	Alkane ν(CH)	ν_s(CH), ν_{as}(CH) observed for CH_2 or CH_3
2750	Aldehyde υ(CH)	sharp, medium intensity

-C≡N, -C≡C-, >C=C=C< Region (2300 cm^{-1} to 2000 cm^{-1})

Frequency (cm^{-1})	Content	Comments
2250	ν(-C≡N)	sharp, weak to med intensity, almost always observed
2150	ν(RC≡CH)	sharp, weak to med intensity, check for ν(C-H) at 3300 cm^{-1}
2260-2190	ν(R-C≡C-R')	sharp, weak to med intensity, observed only for R,R' different
1950	ν(>C=C=C<)	sharp, strong allene

>C=O Region (1800 cm^{-1} to 1650 cm^{-1})

Frequency (cm^{-1})	Content	Comments
1800	Acid chloride	CO Bond order >2
1820,1760	Anhydride	Two peaks are observed

1735	Ester	RCO_2R'
1755	Carbonate	$ROCO_2R'$
1735	Urethane	$ROCONR'_2$
1720	Aldehyde/Ketone	Aldehyde has υ(CH) at 2750 cm^{-1}
1650	Amide	CO Bond Order <2
1630	urea	$R_2NCONR'_2$

C=N, C=C, NO_2 Region (1660 cm^{-1} to 1500 cm^{-1})

Frequency (cm^{-1})	Content	Comments
1690-1640	υ(C=N)	weak to med intensity, sharp
1660-1640	υ(C=C)	weak to med intensity, sharp
1590	υ(NO_2)	strong, sharp

2.8.3 Carbon aliphaticity and aromaticity [25]

Carbon aliphaticity F_{AL-IR} is defined as

(Absorbance around 2920 cm^{-1}) / (Absorbance around 1600 cm^{-1})

And carbon aromaticity F_{Ar-IR} is defined as

(Absorbance around 1600 cm^{-1}) / (Absorbance around 2920 cm^{-1})

The absorbance around 2920 cm^{-1} represents C-H stretching frequency of CH_2 and CH_3 showing presence of aliphatic compounds, while C=C stretching frequency is observed around 1600 cm^{-1} representing aromatic species of different raw coals. The value of F_{Ar-IR} changes with variation in the values of either absorbance of the stretching frequency around 1600 cm^{-1} or 2920 cm^{-1}. The increase in value of F_{Ar-IR} could be attributed either due to an increase in the aromatic content or decrease in the aliphatic content of the coal. Therefore, it follows that even when the absorbance

at aliphatic absorption frequency (aliphatic content) alone decreases without a significant change in aromatic content, the value $F_{Ar\text{-}IR}$ appears to be increasing, while in reality aliphatic content is decreasing without any changes in aromatic content. Thus the value $F_{Ar\text{-}IR}$ always represents the structural changes in coal only in terms of aromatic content of the coal irrespective of whether the actual changes are in aromatic or aliphatic contents and many times it fails to directly indicate the actual changes in the aliphatic content of the coal. So, a new parameter termed as Faliphaticity $F_{AL\text{-}IR}$ is introduced in place of $F_{Ar\text{-}IR}$.

Faliphaticity, $F_{Al\text{-}IR}$ [25]

$F_{Al\text{-}IR}$ = Absorbance around 2920 cm^{-1} / (Absorbance around 2920 cm^{-1} + Absorbance around 1600 cm^{-1})

A $F_{Ar\text{-}IR}$ and $F_{Al\text{-}IR}$ value truly represent the nature of coal or the intrinsic property of coal and is not dependent on the particle size or quantity of coal taken for the measurement of the spectra. According to the formula of Faliphaticity as absorbance around 2920 cm^{-1} increases, it may emit high concentrations of C_4-C_{10} aliphatic hydrocarbons and fire can easily occur under favorable conditions. Thus, the parameter $F_{Al\text{-}IR}$ can be used to evaluate the proneness of the coal for spontaneous heating of coal.

Also, the rate of decrease of $F_{Al\text{-}IR}$ values with increasing temperature is another important property of coal and indicates valuable information about the nature of coal with respect to its spontaneous combustion. Rapid reduction in $F_{Al\text{-}IR}$ values with increase in temperature point out faster emission of hydrocarbons with high concentration or degradation of aliphatic matter of coal. Hence, a coal with high value of $F_{Al\text{-}IR}$ and in addition $F_{Al\text{-}IR}$ decreases at a faster rate with increase in temperature, such a coal is highly prone to spontaneous heating.

CHAPTER – 3

EXPERIMENTAL TECHNIQUES

To study the effects of various parameters of coal that affect the spontaneous heating tendency of coal, the following experiments are needed to be carried out:

- Proximate analysis
- Determination of calorific value
- Determination of Coal Structure with FT-IR Spectroscopy

3.1 SAMPLE COLLECTION AND PREPARATION

It is the process by which the physical and chemical properties of the mineral or ore can be ascertained with the desired accuracy. It is the process of collecting the small portion of a whole such that consistence of that portion represents that of a whole.

Different types of sampling are:

- Channel sampling
- Chip sampling
- Grab sampling
- Bulk sampling
- Drill hole sampling

Chip sampling is done in hard ores where it is difficult to cut the channels. It can be taken in case of uniform ores and where the rock structures are independent of the values. The sample is collected by breaking of small equal sized chips from a face at points usually equally spaced both vertically and horizontally.

Grab sampling is applied to the broken ore in the stope or at the face, ore transported. Usually grab sampling of the ore broken in the stope is unreliable as accurate estimation of the volume of broken ore is impossible. Grab sampling of tubs or ships is however more representations since samples are collected from units of regular volume.

Bulk sampling is done where conventional sampling methods do not give a representative scale; large scale sampling or bulk sampling resorted to. Bulk samples eliminate the effect of irregular distribution of value or minor.

For our Project work, channel sampling method has been carried out which is common among various techniques discussed above.

3.1.1 Channel sampling [14]

The section of seam to be sampled shall be exposed from the roof to the floor. The seam sample shall, be taken in a channel representing the entire cross-section of the seam having the dimensions of 30 x 10 cm, that is, 30 cm in width and 10 cm in depth. For this purpose, two parallel lines, 30 cm apart end at right angles to the bedding planes of the seam shall be marked by a chalked string on the smooth, freshly exposed surface of the seam. Obvious dirt bands exceeding 10 cm in thickness shall be excluded. The channel between the marked chalk lines in the seam shall be cut to a depth of 10 cm and the coal sample collected on a clean strong cloth or tarpaulin placed immediately at the bottom so that the chances of pieces flying off during excavation of coal are minimized.

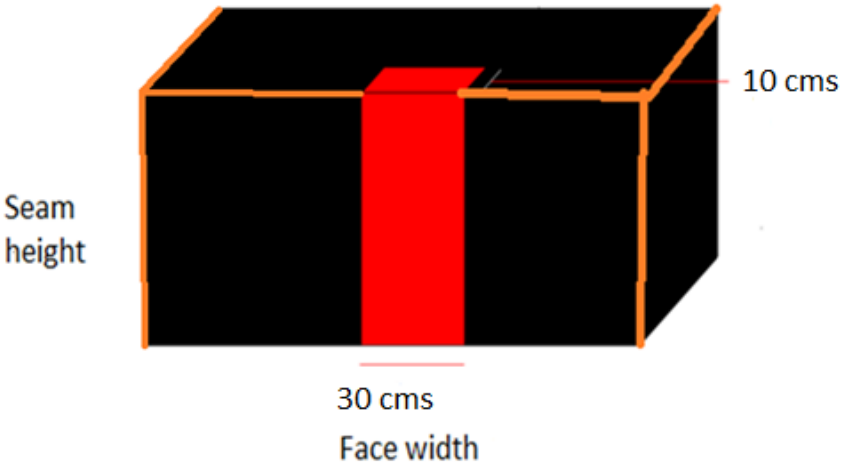


Fig 3.1 Channel Sampling [28]

3.1.2 Sample preparation [14]

The samples received from the field via channel sampling are crushed in the laboratory as per the experimental requirements. The crushed sample is then sieved to required sizes and stored in air tight polythene packets. The packets are stored in air tight containers for further use in experimentation.

3.2 METHODS FOR PROXIMATE ANALYSIS OF COAL

Proximate analysis [13]

Proximate analysis of coal is a method to determine the distribution of various constituents such as moisture, volatile matter, ash and fixed carbon. The method determined by IS (Indian Standard) 1350 (Part- I)-1984 is followed for proximate analysis, i.e. for the determination of volatile matter, moisture, fixed carbon and ash.

Determination of Moisture Content (M) [13]

Moisture present in coal can classified into two types:

1) Extraneous moisture,
2) Inherent moisture

Extraneous moisture easily evaporates when exposed to sunlight while inherent moisture can be removed by heating for 90 minutes at 105^0 C. The mode of occurrence and handling of coal is responsible for the quantity of external moisture but the air-dried moisture is associated with the inherent hygroscopic nature of the coal.

Procedure

- About 1g of air-dried coal sample finely powdered (-212μ) and weighed over a silica crucible.
- It is placed inside an electric hot air oven (Plate 3.1) which was maintained at 105^0C and allowed to remain there 90 minutes.
- It was taken out with a pair of tongues, and cooled inside desiccators for about 15 minutes and the weight is taken.
- The loss in weight was reported as moisture (on percentage basis).

Moisture is calculated as per the following formula.

$$\% \text{ Moisture} = (Y-Z/Y-X) *100$$

Where,

X= weight of empty crucible, g

Y= weight of crucible and coal sample before heating, g

Z= weight of crucible and coal sample after heating, g

Plate 3.1 Oven for Moisture Content Determination

Determination of Ash Content (A) [13]

The residue left after the combustion of coal under some specified conditions is called the coal ash. It is formed as the result of chemical changes that take place in the mineral matter and does not occur as such in coal. Hence ash and mineral matter of coal are not identical. Two types of ash forming materials in coal are mainly the extraneous and inherent mineral matters.

Procedure:

The empty crucible was cleaned by heating in a muffle furnace for one hour at 800^0 C so that other mineral matter if presents get burnt. It was taken out, cooled to room temperature and the weight is taken. Approximately 1g of coal sample was weighed in the crucible and placed in a muffle furnace at 450^0 C for 30 minutes and the temperature of the furnace was raised to 850^0 C for 1hour. The crucible was taken out and placed in desiccators and weighed.

Ash is calculated as per the following formula:

$$\% \text{ Ash} = (Z\text{-}X/Y\text{-}X) *100$$

Where,

X = weight of empty crucible in g

Y = weight of coal sample and crucible in g (Before heating)

Z = weight of coal sample and crucible in g (After heating)

Plate 3.2 Muffle Furnance for Determination of Volatile Matter and Ash Content

Determination of Volatile Matter (VM) [13]

When a coal sample is heated in specified equipment's under prescribed conditions in Indian standard, the loss of mass in coal, corrected for moisture, is referred to as volatile matter of coal. Some of the components of coal transformed to volatile matter are hydrogen, carbon monoxide, methane and other hydrocarbons, vapors, ammonia, some organic sulphur and oxygen containing deepens and some incombustible gases, such as CO and water vapor, all of which come from the disintegration of organic matter in coal. Inorganic materials in coal are responsible for the presence of the water of hydration of mineral matter, carbon dioxide from carbonates and hydrogen chloride from inorganic chlorides to the volatile matter.

Procedure

For the determination of volatile matter a special volatile matter silica crucible (38 mm height, 25 mm external diameter and 22 mm internal diameter) was used. The empty volatile matter crucible was weighed. 1g of coal sample (-212μ size) was weighed in the volatile matter crucible and it was placed inside a muffle furnace maintained at 925^{o} C with the lid covering the crucible for 7 minutes. The heating was carried in the muffle furnace (Plate 3.2) out exactly for seven minutes, after which the crucible was removed, cooled in air, then in desiccators and weighed again. The calculation was done as per the following formula:

$$\% \text{ Volatile Matter} = (Y\text{-}Z/Y\text{-}X)*100 - \% \text{ Moisture}$$

Where,

X = weight of empty crucible, g

Y = weight of crucible and coal sample before heating, g

Z = weight of crucible and coal sample after heating, g

Determination of Fixed Carbon (FC)

After the determination of moisture, volatile matter and ash the mathematical remaining is fixed carbon by definition. Fixed carbon plus ash present the approximate yield of coke from coal. The value of fixed carbon is evaluated by subtracting the resultant summation of moisture (M), volatile matter (VM) and ash (A) from 100 with all parts on the same moisture reference basis

$$FC=100 - \% (M+VM+A)$$

3.3 DETERMINATION OF GROSS CALORIFIC VALUE [28]

The calorific value of coal is the amount of potential energy in coal that can be changed into actual heating ability. The value can be estimated and compared with different grades of coal or even other materials.

Materials of different grades will produce differing quantities of heat for a given mass. The calorific value of coal is commonly determined by the bomb calorimeter method. This apparatus consists of a cylindrical chamber known as bomb and it is made up of stainless steel. This chamber is equipped with an air tight cover which can be screwed on the chamber. There are three terminals; two for sparking and one for the entry of oxygen. After forcing the oxygen into the chamber the enactment can be blocked by screwing in the third terminal.

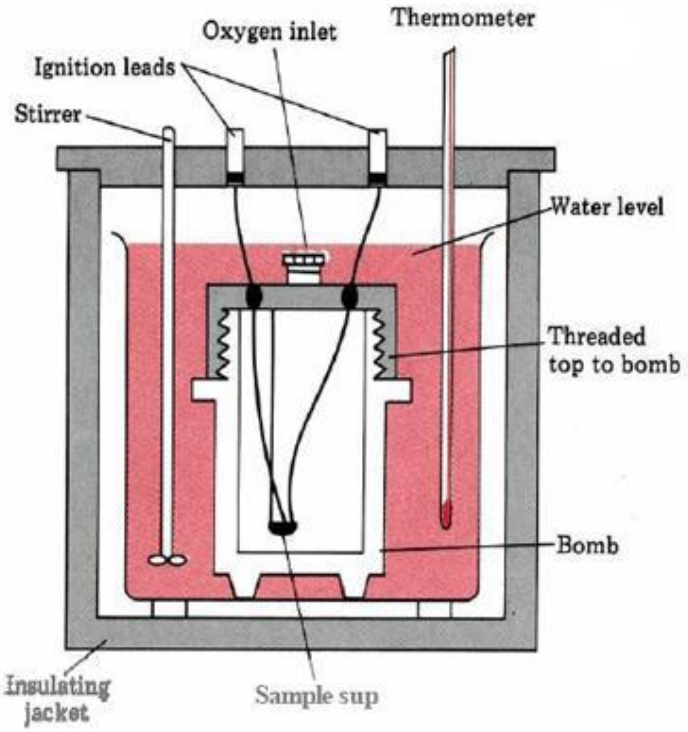


Fig 3.2 Bomb Calorimeter [28]

On the other side of the cover, there are two bent rods connected to two ends. The bent rods have small holes through which two fuse wires are connected. There is the provision for putting the crucible containing the pellet tied to the fuse wire by means of a cotton thread. This whole set-up

is placed in a bigger vessel holding a quantity of water in it. A stirrer is used for stirring the water in the bigger vessel.

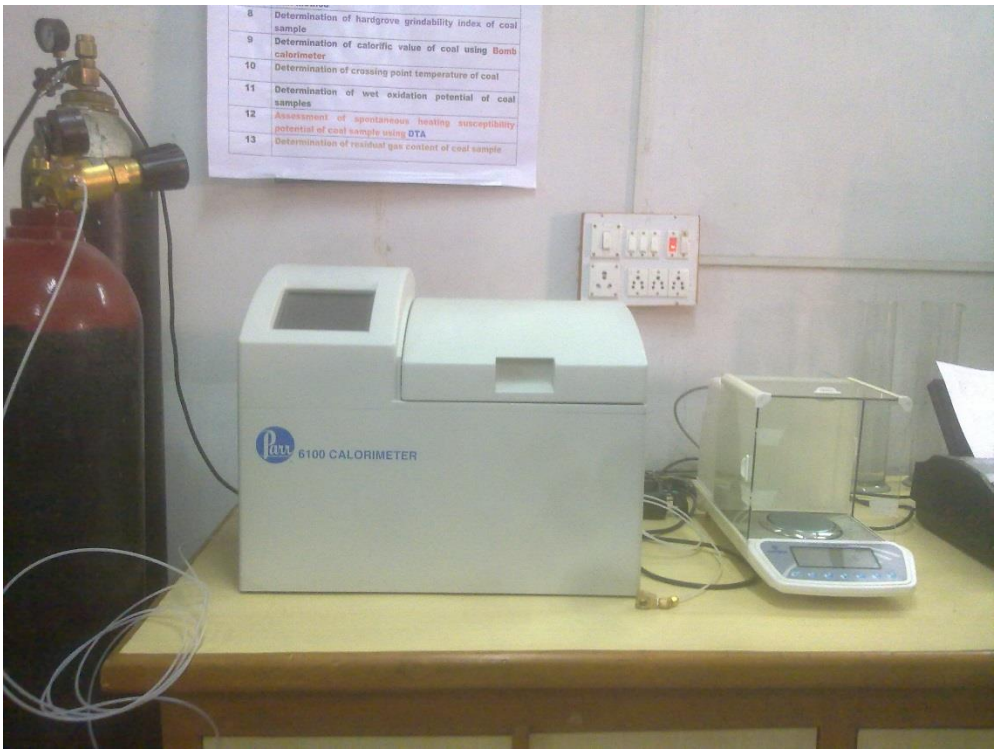


Plate 3.3 Digital Bomb Calorimeter

Procedure:

1g of air dried coal sample is taken by weighing in a balance of - 212 micron (-72 mesh BSS). A pellet is made with the coal and weighed. The calorimeter cover is taken and about 10 ml/min of distilled water is poured into it. The pellet in the crucible is brought in contact with the fuse wire by means of a thread. The cover is then tightened. Oxygen is then admitted into the calorimeter at a pressure of about 300 - 400 psi atmospheres. Then 2L of water is put into the bigger vessel. Necessary electrical connections are made and stirrer is adjusted in the adjusted position. The stirring is done softly for 5 minutes. The initial temperature reading is then taken. A sparking and combustion of coal has taken place in the calorimeter after the fire of bomb. The maximum reached temperature is then noticed. The bomb is removed and the pressure exhausted. The bomb internal is examined for unburnt or sooty deposits. If such material is found, then the test is discarded.

The calorific value of coal is calculated by:

Calorific value = ($T_2 – T_1$) * Water equivalent / Weight of the pellet

Where,

T_1 – Initial temperature, T_2 – Final temperature

The following formula designed by CFRI (Central Fuel Research Institute) [28]:

If M < 2% then Useful heat value (UHV) =91.7F+75.6(V-0.1A)-60M

If M > 2% then Useful heat value (UHV) =85.6[100-(1.1A+M)-60M]

Where, F=Fixed Carbon, V=Volatile Matter, A=Ash, M=Moisture

TABLE 3.1 GRADING OF NON-COKING COAL [27]

As per the Gazette Notification No. 22021/1/2008-CRC-II, DT. 30.12.2011 issued by Government of India to switch over from UHV based gradation system to GCV based system and in pursuance of the Colliery Control Order 2000.

GRADE	GROSS CALORIFIC VALUE(Kcal/kg)
G1	Exceeding 7000
G2	Exceeding 6700 and not exceeding 7000
G3	Exceeding 6400 and not exceeding 6700
G4	Exceeding 6100 and not exceeding 6400
G5	Exceeding 5800 and not exceeding 6100
G6	Exceeding 5500 and not exceeding 5800
G7	Exceeding 5200 and not exceeding 5500
G8	Exceeding 4900 and not exceeding 5200
G9	Exceeding 4600 and not exceeding 4900
G10	Exceeding 4300 and not exceeding 4600
G11	Exceeding 4000 and not exceeding 4300

G12	Exceeding 3700 and not exceeding 4000
G13	Exceeding 3400 and not exceeding 3700
G14	Exceeding 3100 and not exceeding 3400
G15	Exceeding 2800 and not exceeding 3100
G16	Exceeding 2500 and not exceeding 2800
G17	Exceeding 2200 and not exceeding 2500

TABLE 3.2 GRADING OF COKING COAL

GRADE	**ASH CONTENT**
STEEL GRADE – I	< 15 %
STEEL GRADE – II	15 – 18 %
WASHERY GRADE – I	18 – 21 %
WASHERY GRADE – II	21 – 24 %
WASHERY GRADE – III	24 – 28 %
WASHERY GRADE – IV	28 – 35%
SEMI COKING – I	< 19 %(A+M)
SEMI COKING – II	19 – 24 %(A+M)
HARD COKE BY PRODUCT PREMIUM	< 25%
ORDINARY	25 – 30%
BEEHIVE PREMIUM	< 27 %
BEEHIVE SUPERIOR	27 – 31 %
BEEHIVE ORDINARY	32 – 36%

3.4 STRUCTURE OF COAL USING FT-IR SPECTROSCOPY

The FT-IR spectra of raw coals were taken using model Perkin Emler Spectrum two with Lithium Tansalate detector and a beam splitter-KBR. The spectra of coal sample were taken in a range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1}.

In FT-IR spectroscopy of coal, the coal sample is mixed with potassium bromide (KBr) in the ratio 1:10. So to normalize the effect of KBr in the scanning of coal samples, a background pellet of KBr is scanned before the scanning of coal samples to provide a baseline for the coal samples.

Procedure

- Coal samples are crushed to a fine size.
- 1mg of coal sample is thoroughly mixed with 10mg of KBr powder to get the required homogenous mixture (The first sample should only contain KBr powder to create a background for scanning of successive coal samples).
- Now the required sample is uniformly spread over the platens of pellet holder.
- Hydraulic press is used for making a coal pellet at required pressure.

Plate 3.4 Hydraulic Press

- The pellet is taken out of the holder and kept in desiccators before taking the spectra.

- At last, the pellet is loaded over the FT-IR instrument and spectra of coal sample is observed.

Plate 3.5 FT-IR Spectroscopy

CHAPTER – 4

RESULTS AND ANALYSIS

EXPERIMENTAL SPECIFICATIONS

1. Proximate analysis

A. Determination of moisture

- Amount of coal: 1 g coal
- Size of coal:-72 mesh size
- Heating time: 1.5 hours at 110° C

B. Determination of volatile matter

- Amount of coal: 1 g of coal
- Size of coal: -72 mesh size
- Heating time: 7 minutes at 925° C

C. Determination of ash

- Amount of coal: 1 g of coal sample
- Size of coal: - 72 mesh size
- Heating time: 30 minutes at 450°C and 60 minutes at 850° C

2. Gross Calorific Value

- Amount of coal: 1 g coal
- Size of coal:-72 mesh size
- Heating time: 30 minutes at 40° C
- Oxygen flow rate: 300-400 psi atmosphere

3. Coal Structure using FT-IR Spectroscopy

- Amount of coal: 1 mg coal
- Size of coal:-72 mesh size

LIST OF COAL SAMPLES

Sample collection is a vital process of the project. It includes the collection of the sample in a designated manner. It is the course of collecting the small portion of a whole, which represents the consistence of that portion and characterizes a whole seam. The method used for the collection of the sample was channel sampling. The samples were collected from different coalfield of India, given in the Table 4.1 using channel sampling method and were crushed into required size, in the laboratory in accordance with the experimental necessities.

TABLE 4.1 LIST OF COAL SAMPLES

Sl.No.	Sample Id	Name of Organization
1	MCL - 1	MAHANADI COALFIELDS LTD (MCL)
2	MCL – 2	
3	MCL - 3	
4	MCL – 4	
5	MCL - 5	
6	MCL - 6	
7	MCL - 7	
8	CCL – 1	CENTRAL COALFIELDS LTD (CCL)
9	CCL – 2	
10	CCL – 3	
11	CCL – 4	
12	BCCL – 1	BHARAT COKING COAL LTD (BCCL)
13	BCCL – 2	
14	BCCL – 3	
15	BCCL – 4	

16	BCCL – 5	
17	NEC – 1	NORTH-EASTERN COALFIELDS (NEC)
18	NEC – 2	
19	SCCL-1	SINGARENI COAL COMPANY LTD (SCCL)
20	SECL – 1	SOUTH EASTERN COALFIELDS LTD (SECL)

PROXIMATE ANALYSIS PARAMETERS OF COAL

The proximate analysis is a part of determination of intrinsic properties of the coal. It is a substantial part of the process of experimentation carried out to determine any property of the coal. The sole purpose of coal proximate analysis is to ascertain the intrinsic parameters of coal like, fixed carbon (FC), volatile matters (VM), moisture content (M), and ash of the coal sample. The measurement is done on weight percent (wt. %) and the calculation is completed in a number of different basis. The proximate analysis of coal sample is given in Table 4.2.

TABLE 4.2 RESULT OF PROXIMATE ANALYSIS

Sample Id	Moisture (%)	Volatile matter (%)	Ash (%)	Fixed Carbon (%)
MCL – 1	8.52	11.08	36.6	43.8
MCL – 2	3.12	29.7	24.1	43.08
MCL – 3	4.32	35.82	18	41.86
MCL – 4	9.1	22.97	27.3	40.63
MCL – 5	8.2	25.9	19.76	46.14
MCL – 6	7.4	23.4	23.48	45.72
MCL – 7	6.94	24.45	24.89	43.72
CCL – 1	6.39	17.63	34.5	41.48

CCL - 2	8.3	21.44	36.7	33.56
CCL – 3	4.8	23.37	31.59	40.24
CCL – 4	3.46	23.06	32.63	40.71
BCCL – 1	0.31	10.45	12.45	76.79
BCCL – 2	0.47	11.91	13.17	74.45
BCCL – 3	2.48	12.76	14.81	69.95
BCCL – 4	0.58	10.66	12.86	75.9
BCCL – 5	0.89	14.95	26.84	57.32
NEC – 1	3.17	13.46	31.19	52.18
NEC – 2	12.33	14.66	33.48	39.53
SCCL – 1	6.97	19.86	18.26	54.91
SECL – 1	6.8	20.45	26.87	45.88

GROSS CALORIFIC VALUE

Calorific value is the amount of energy released by the coal, by burning the unit of material. It is trapped in the form of the potential energy, which can be converted into heat energy. Gradation of the material is done by the amount of heat energy produced by the unit mass of the material. For determination of calorific value of coal, automatic bomb calorimeter is used. The Bomb calorimeter comprises of a resolute cylindrical chamber recognized as bomb, which is made up of stainless steel. The chamber in which bomb is kept is built-in with an air tight cover which can be made to screw on the chamber. The GCV of all the collected coal samples are listed in Table 4.3.

TABLE 4.3 RESULT OF GROSS CALORIFIC VALUE (KCal/Kg)

Sl.No.	Sample Id	Grade	GCV (in KCal/Kg)
1	MCL – 1	G13	3517.99
2	MCL – 2	G13	5923.73
3	MCL – 3	G4	6259.81
4	MCL – 4	G8	4968.26
5	MCL – 5	G12	3758.78
6	MCL - 6	G10	4370.11
7	MCL - 7	G12	3859.47
8	CCL – 1	G6	5699.70
9	CCL - 2	G1	6076.54
10	CCL – 3	G10	4325.81
11	CCL – 4	G9	4732.54
12	BCCL – 1	STEEL GRADE 1	9100.63
13	BCCL – 2	STEEL GRADE 1	8327.46
14	BCCL – 3	STEEL GRADE 1	8137.48
15	BCCL – 4	STEEL GRADE 1	8700.48
16	BCCL – 5	G3	6532.88
17	NEC – 1	G1	7869.33
18	NEC – 2	G2	6749.33
19	SCCL – 1	G6	5689.13
20	SECL – 1	G7	5342.96

ABSORBANCE AND FALIPHATICITY OF COAL

TABLE 4.4 ABSORBANCE AT 2920 cm^{-1}, 1600 cm^{-1} AND F_{Al-IR} OF RAW COAL

Sl.No.	Sample Id	A(2920 cm^{-1})	A(1600 cm^{-1})	F_{Al-IR}
1	MCL – 1	0.3717	0.2593	0.5891
2	MCL – 2	0.5834	0.4407	0.5697
3	MCL – 3	0.2915	0.5387	0.3511
4	MCL – 4	2.1007	2.3098	0.4763
5	MCL – 5	1.9308	1.5406	0.5562
6	MCL – 6	1.0926	0.9531	0.5341
7	MCL - 7	1.4136	1.1580	0.5497
8	CCL - 1	0.7039	1.1034	0.3895
9	CCL – 2	0.8295	2.075	0.2856
10	CCL – 3	1.6418	1.3840	0.5426
11	CCL – 4	2.3493	2.2365	0.5123
12	BCCL – 1	0.4504	1.398	0.2437
13	BCCL – 2	0.3677	1.0241	0.2642
14	BCCL – 3	0.4995	1.2247	0.2897
15	BCCL – 4	0.4336	1.2557	0.2567
16	BCCL – 5	0.4726	0.9412	0.3343
17	NEC - 1	0.3889	0.8483	0.3143
18	NEC – 2	0.5846	1.2048	0.3267
19	SCCL – 1	0.8027	1.1255	0.4163
20	SECL – 1	0.7177	0.9726	0.4246

TABLE 4.5 ABSORBANCE AT 2920 cm^{-1}, 1600 cm^{-1} AND $F_{Al\text{-}IR}$ AT 100º C

Sl.No.	Sample Id	A(2920 cm^{-1})	A(1600 cm^{-1})	$F_{Al\text{-}IR}$
1	MCL – 1	0.3266	0.2602	0.5566
2	MCL – 2	0.5175	0.4419	0.5394
3	MCL – 3	0.2735	0.5391	0.3366
4	MCL – 4	1.9193	2.3101	0.4538
5	MCL – 5	1.7209	1.5421	0.5274
6	MCL – 6	0.9873	0.9539	0.5086
7	MCL - 7	1.2652	1.1586	0.5220
8	CCL - 1	0.6615	1.1096	0.3735
9	CCL – 2	0.8007	2.091	0.2769
10	CCL – 3	1.4772	1.3851	0.5161
11	CCL – 4	2.1345	2.2368	0.4883
12	BCCL – 1	0.4410	1.389	0.2410
13	BCCL – 2	0.3558	1.0261	0.2575
14	BCCL – 3	0.4807	1.2361	0.2800
15	BCCL – 4	0.4332	1.286	0.2520
16	BCCL – 5	0.4455	0.9432	0.3208
17	NEC - 1	0.3701	0.8493	0.3035
18	NEC – 2	0.5523	1.2056	0.3142
19	SCCL – 1	0.7453	1.1259	0.3983
20	SECL – 1	0.6586	0.9733	0.4036

TABLE 4.6 ABSORBANCE AT 2920 cm^{-1}, 1600 cm^{-1} AND $F_{Al\text{-}IR}$ AT 200° C

Sl.No.	Sample Id	A(2920 cm^{-1})	A(1600 cm^{-1})	$F_{Al\text{-}IR}$
1	MCL – 1	0.2980	0.2657	0.5286
2	MCL – 2	0.4694	0.4431	0.5144
3	MCL – 3	0.2625	0.5402	0.3270
4	MCL – 4	1.8007	2.3143	0.4376
5	MCL – 5	1.5706	1.5463	0.5039
6	MCL – 6	0.9206	0.9567	0.4904
7	MCL - 7	1.1637	1.1591	0.5010
8	CCL - 1	0.6313	1.1103	0.3625
9	CCL – 2	0.7873	2.101	0.2726
10	CCL – 3	1.3716	1.3882	0.4970
11	CCL – 4	1.9947	2.2385	0.4712
12	BCCL – 1	0.4401	1.397	0.2399
13	BCCL – 2	0.3551	1.042	0.2544
14	BCCL – 3	0.4682	1.2375	0.2745
15	BCCL – 4	0.4312	1.295	0.2498
16	BCCL – 5	0.4294	0.9475	0.3119
17	NEC - 1	0.3588	0.8502	0.2968
18	NEC – 2	0.5335	1.2077	0.3064
19	SCCL – 1	0.7095	1.1287	0.3860
20	SECL – 1	0.6228	0.9762	0.3895

TABLE 4.7 ABSORBANCE AT 2920 cm^{-1}, 1600 cm^{-1} AND $F_{Al\text{-}IR}$ AT 300º C

Sl.No.	Sample Id	A(2920 cm^{-1})	A(1600 cm^{-1})	$F_{Al\text{-}IR}$
1	MCL – 1	0.2756	0.2663	0.5086
2	MCL – 2	0.4358	0.4439	0.4954
3	MCL – 3	0.2523	0.5412	0.3180
4	MCL – 4	1.7084	2.3151	0.4246
5	MCL – 5	1.4619	1.5468	0.4859
6	MCL – 6	0.8672	0.9569	0.4754
7	MCL - 7	1.0876	1.1596	0.4840
8	CCL - 1	0.6055	1.1123	0.3525
9	CCL – 2	0.7745	2.109	0.2686
10	CCL – 3	1.2870	1.3887	0.4810
11	CCL – 4	1.8860	2.2391	0.4572
12	BCCL – 1	0.4391	1.399	0.2389
13	BCCL – 2	0.3509	1.045	0.2514
14	BCCL – 3	0.4568	1.2381	0.2695
15	BCCL – 4	0.4276	1.298	0.2478
16	BCCL – 5	0.4139	0.9482	0.3039
17	NEC – 1	0.3489	0.8511	0.2908
18	NEC – 2	0.5163	1.2081	0.2994
19	SCCL – 1	0.6775	1.1291	0.3750
20	SECL – 1	0.5925	0.9772	0.3775

TABLE 4.8 ABSORBANCE AT 2920 cm^{-1}, 1600 cm^{-1} AND $F_{Al\text{-}IR}$ AT 400º C

Sl.No.	Sample Id	A(2920 cm^{-1})	A(1600 cm^{-1})	$F_{Al\text{-}IR}$
1	MCL – 1	0.2553	0.2672	0.4886
2	MCL – 2	0.4049	0.4451	0.4764
3	MCL – 3	0.2424	0.5421	0.3090
4	MCL – 4	1.6203	2.3164	0.4116
5	MCL – 5	1.3606	1.5473	0.4679
6	MCL – 6	0.8171	0.9577	0.4604
7	MCL - 7	1.0165	1.1602	0.4670
8	CCL - 1	0.5799	1.1133	0.3425
9	CCL – 2	0.7613	2.116	0.2646
10	CCL – 3	1.2077	1.3895	0.4650
11	CCL – 4	1.7827	2.2397	0.4432
12	BCCL – 1	0.4373	1.401	0.2379
13	BCCL – 2	0.3490	1.056	0.2484
14	BCCL – 3	0.4492	1.2395	0.2660
15	BCCL – 4	0.4243	1.302	0.2458
16	BCCL – 5	0.3897	0.9487	0.2959
17	NEC – 1	0.3393	0.8521	0.2848
18	NEC - 2	0.4998	1.2096	0.2924
19	SCCL – 1	0.6470	1.1306	0.3640
20	SECL – 1	0.5635	0.9783	0.3655

CORRELATION STUDY

Correlation between intrinsic properties of coal sample and spontaneous heating liability were carried to find out relationship between them. The correlation analysis was carried out using MS Excel 2013. Microsoft Excel 2013 provides efficient tools to analyze large amount of data with ease.

TABLE 4.9 CORRELATION BETWEEN FALIPHATICITY AND PROPERTIES OF COAL

SL.NO.	INDEPENDENT VARIABLE	EMPERICAL RELATION	R^2
1	MIOSTURE (M)	$F_{Al\text{-}IR} = -70.803M^2 + 76.225M - 13.397$	0.5269
2	ASH (A)	$F_{Al\text{-}IR} = -752.7A^2 + 564.93A - 75.607$	0.2898
3	VOLATILE MATTER (VM)	$F_{Al\text{-}IR} = 0.0015VM^2 - 0.0377VM + 0.5928$	0.2396
4	GROSS CALORIFIC VALUE (GCV)	$F_{Al\text{-}IR} = 6E\text{-}09\ GCV^2 - 0.0001GCV + 1.0031$	0.8361

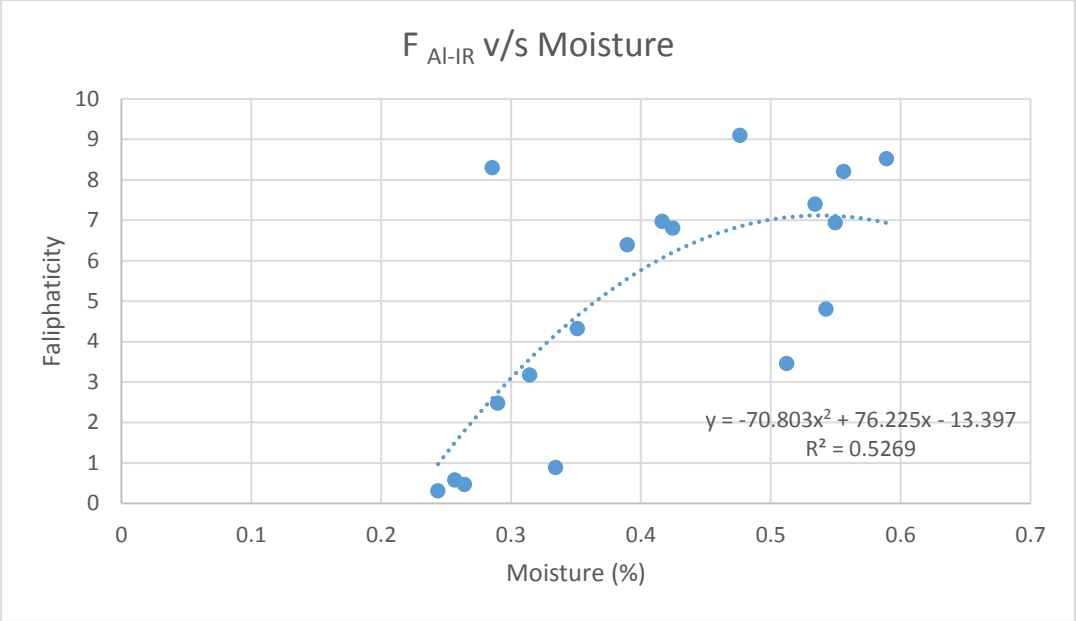


Fig 4.1 Correlation of Faliphaticity with moisture

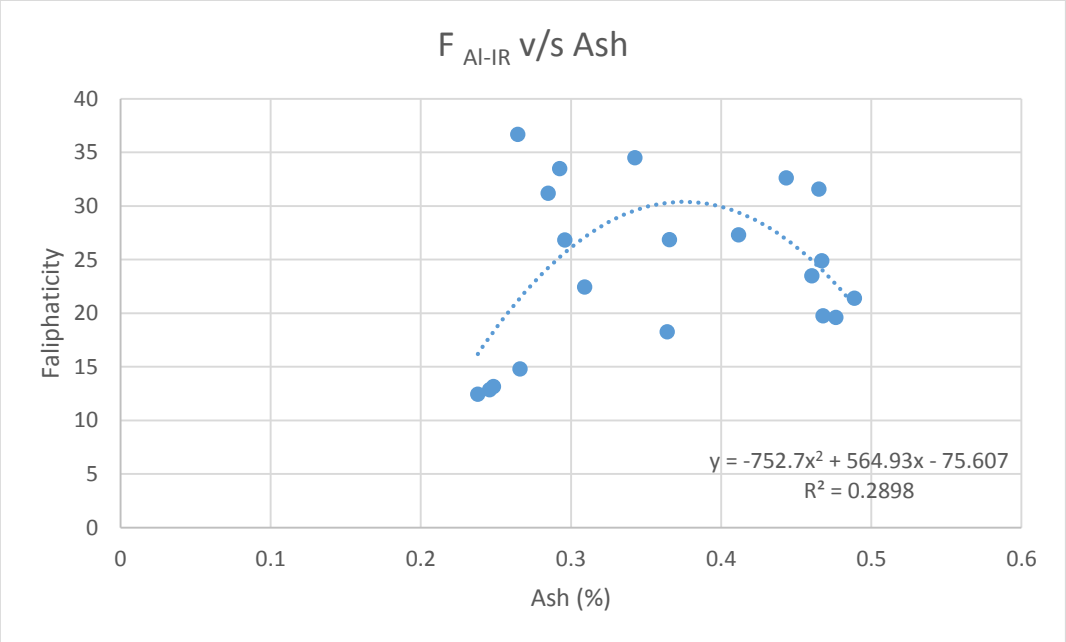


Fig 4.2 Correlation of Faliphaticity with ash content

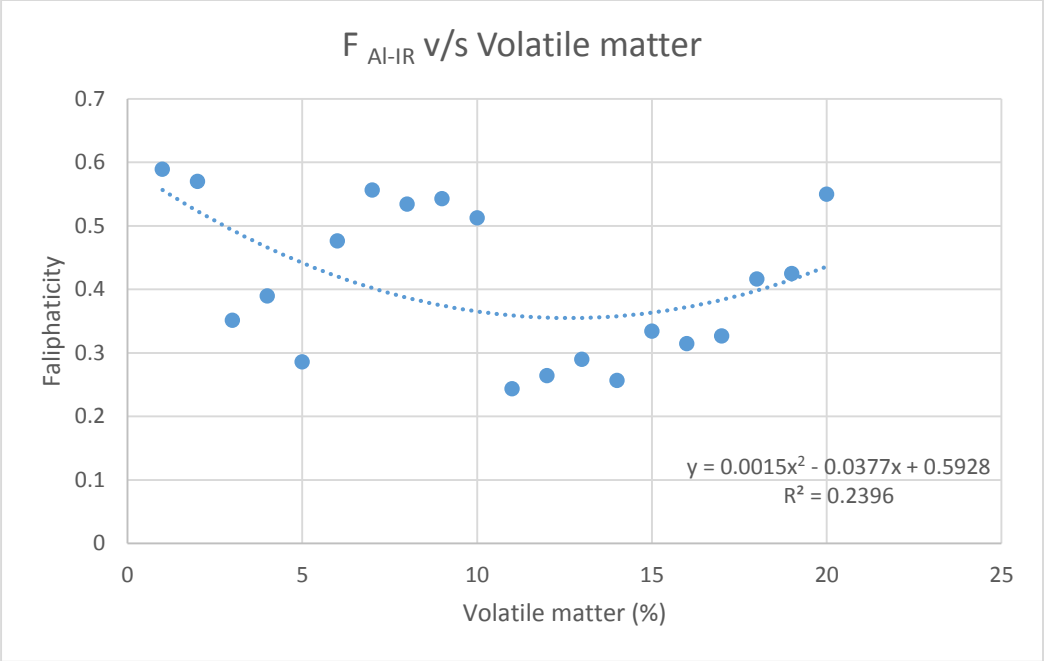


Fig 4.3 Correlation of Faliphaticity with volatile matter

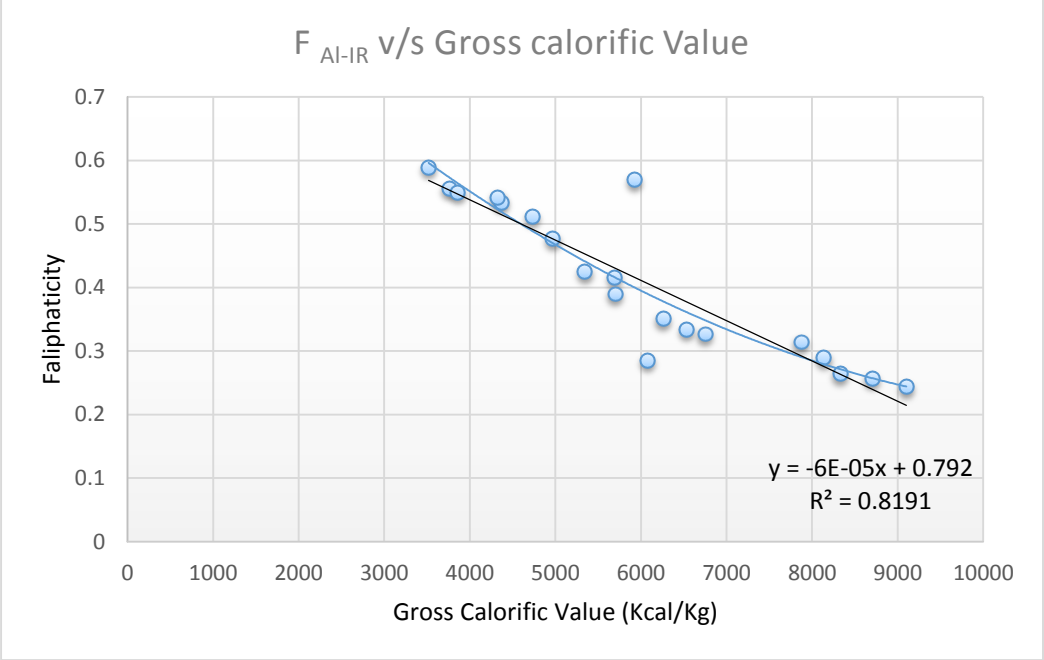


Fig 4.4 Correlation of Faliphaticity with Gross calorific value

CHAPTER 5

CONCLUSIONS

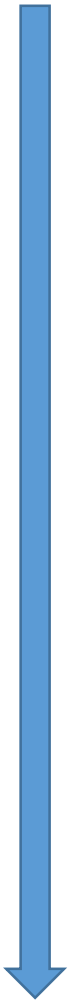
The conclusions are drawn based on the experimental investigations and analysis and are summarized below:

- The absorbance of coal sample, around 2920 cm^{-1} is found to be gradually decreasing with increase in temperature.
- The absorbance of coal sample, around 1600 cm^{-1} is found to remain relatively constant or slightly increasing with an increase in temperature. This concludes that with rise in temperature aromatic content of coal approximately remains constant.
- From FT-IR Spectroscopy it is found that coal sample from MCL is most liable to spontaneous heating and the coal from BCCL is poorly liable to spontaneous heating.
- From the correlation analysis it is also found that with increase in moisture and volatile matter Faliphaticity decreases while it's reverse in case of ash.
- With the increase in ash percentage the spontaneous heating susceptibility decreases and vice-versa.
- While with increase in volatile matter in the coal the spontaneous heating susceptibility increase and vice versa.
- Spontaneous heating liability of the collected coal based on the results of faliphaticity using FT-IR are shown in Table 5.1.
- Faliphaticity of coal shows better trend with gross calorific value

$$F_{Al\text{-}IR} = -6E\text{-}05\ GCV + 0.792 \text{ and } R^2 = 0.8191$$

5.1 SPONTANEOUS HEATING LIABILITY AS PER FALIPHATICITY

HIGHLY LIABLE TO SPONTANOUS HEATING



POORLY LIABLE TO SPONTANEOUS HEATING

Sl.No.	Sample Id	Faliphaticity
1	MCL – 1	0.5891
2	MCL – 2	0.5697
3	MCL - 5	0.5562
4	MCL – 7	0.5497
5	CCL – 3	0.5426
6	MCL – 6	0.5341
7	CCL - 4	0.5123
8	MCL – 4	0.4763
9	SECL – 1	0.4246
10	SCCL – 1	0.4163
11	CCL – 1	0.3895
12	MCL – 3	0.3511
13	BCCL – 5	0.3343
14	NEC – 2	0.3267
15	NEC – 1	0.3143
16	BCCL – 3	0.2897
17	CCL – 2	0.2856
18	BCCL – 2	0.2642
19	BCCL – 4	0.2567
20	BCCL - 11	0.2437

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APPENDIX –1

CURVES OF FT-IR SPECTROSCOPY AT VARIOUS TEMPERATURES

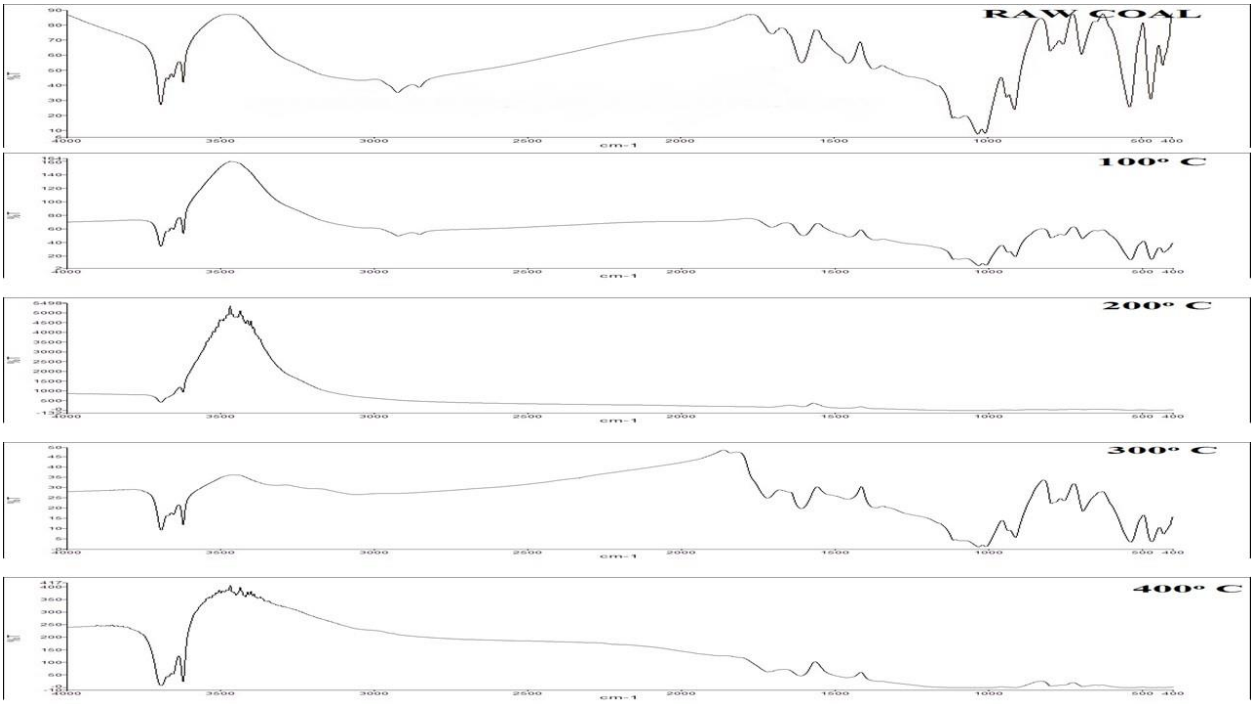

Fig A1.1 Comparison of FT-IR Spectrum at various temperatures, MCL – 01.

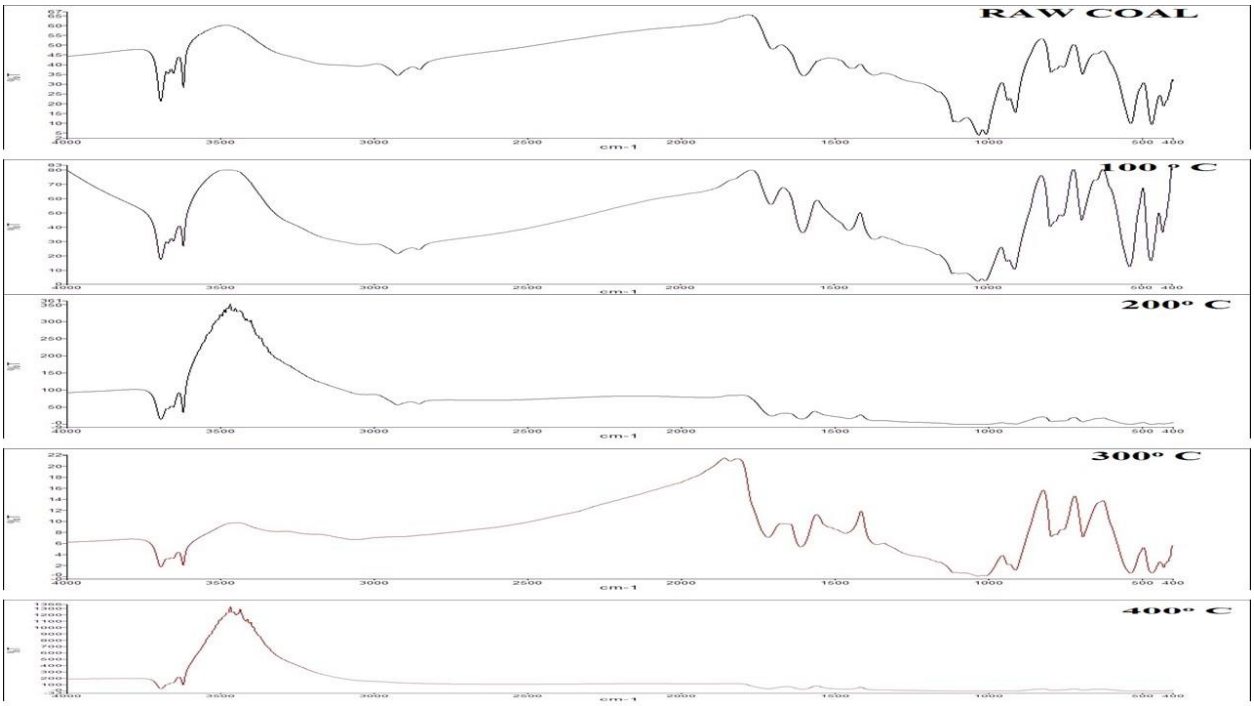

Fig A1.2 Comparison of FT-IR Spectrum at various temperatures, MCL – 02.

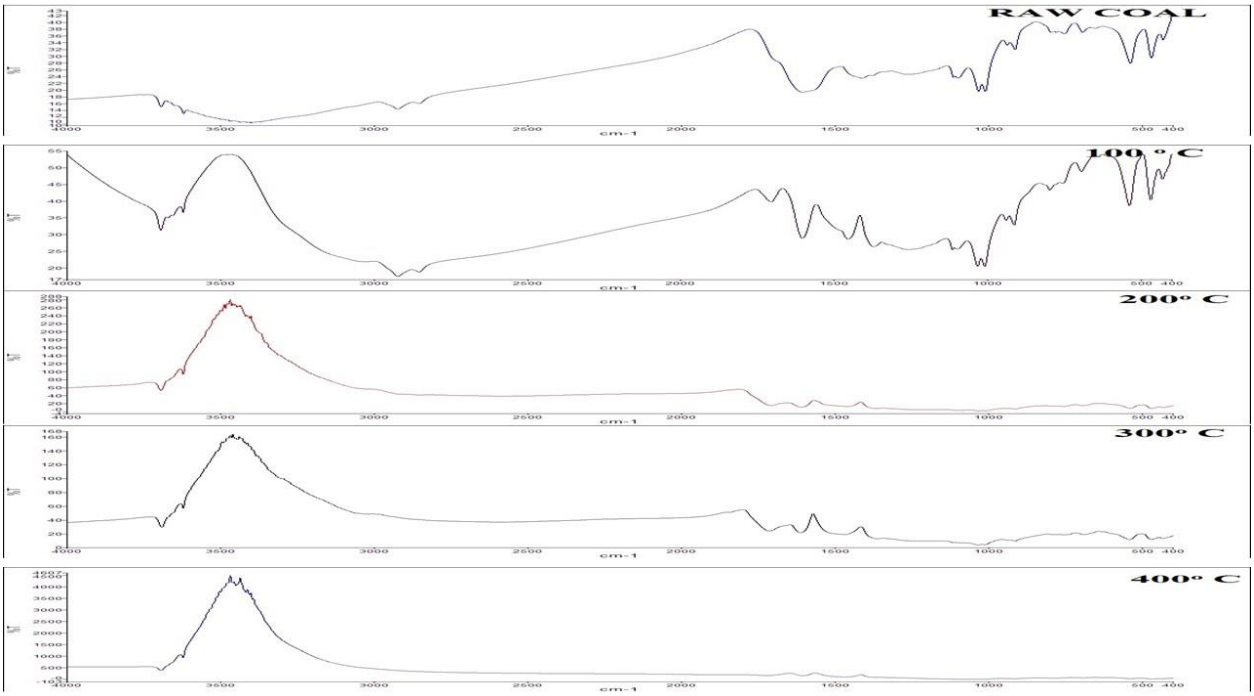

Fig A1.3 Comparison of FT-IR Spectrum at various temperatures, MCL – 03.

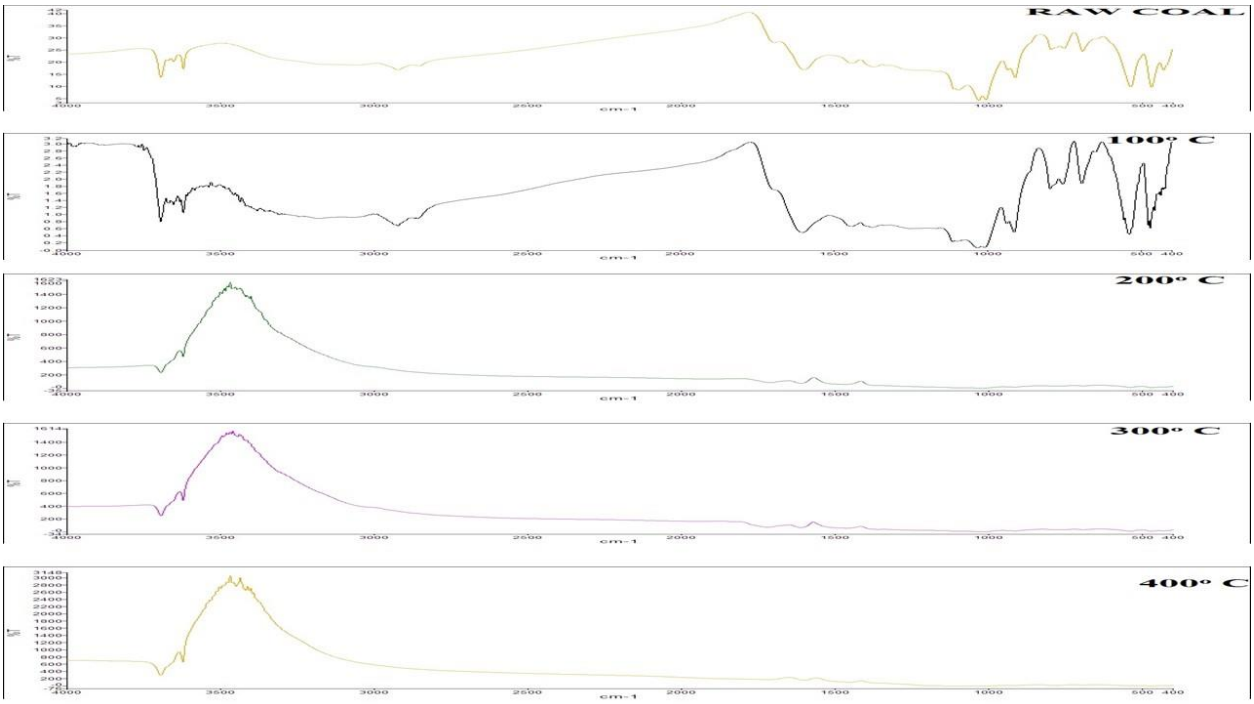

Fig A1.4 Comparison of FT-IR Spectrum at various temperatures, MCL – 04.

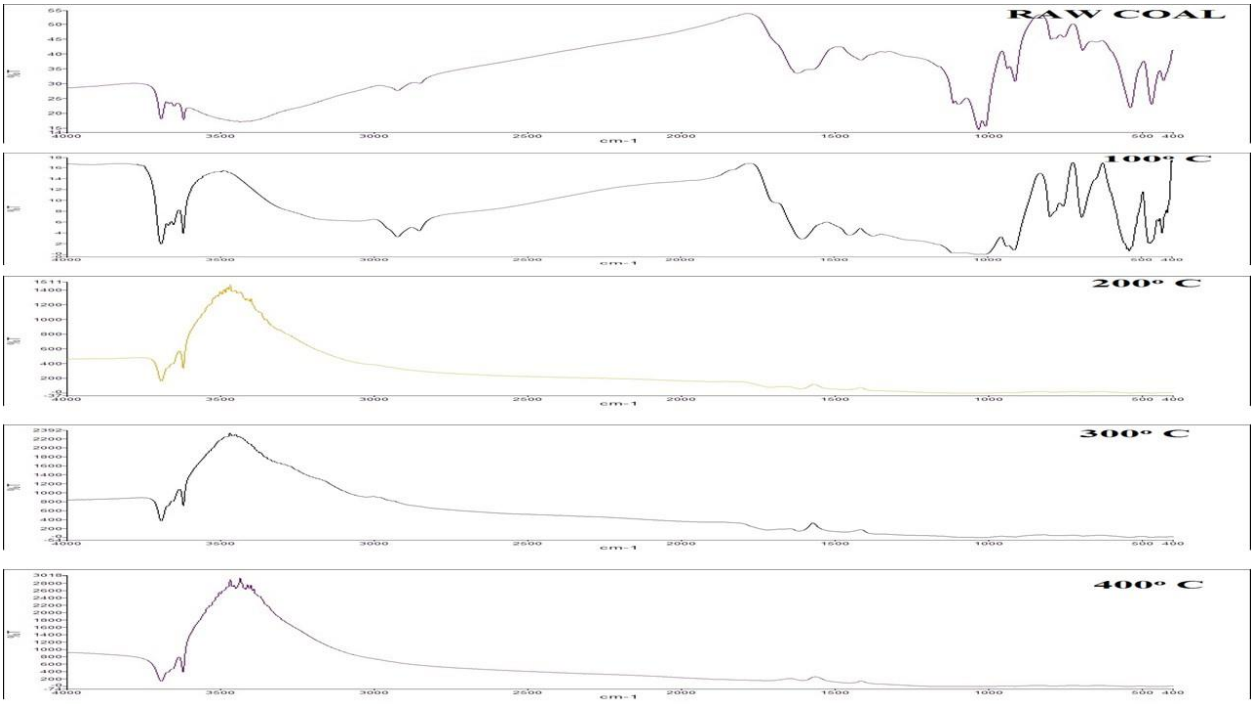

Fig A1.5 Comparison of FT-IR Spectrum at various temperatures, MCL – 05.

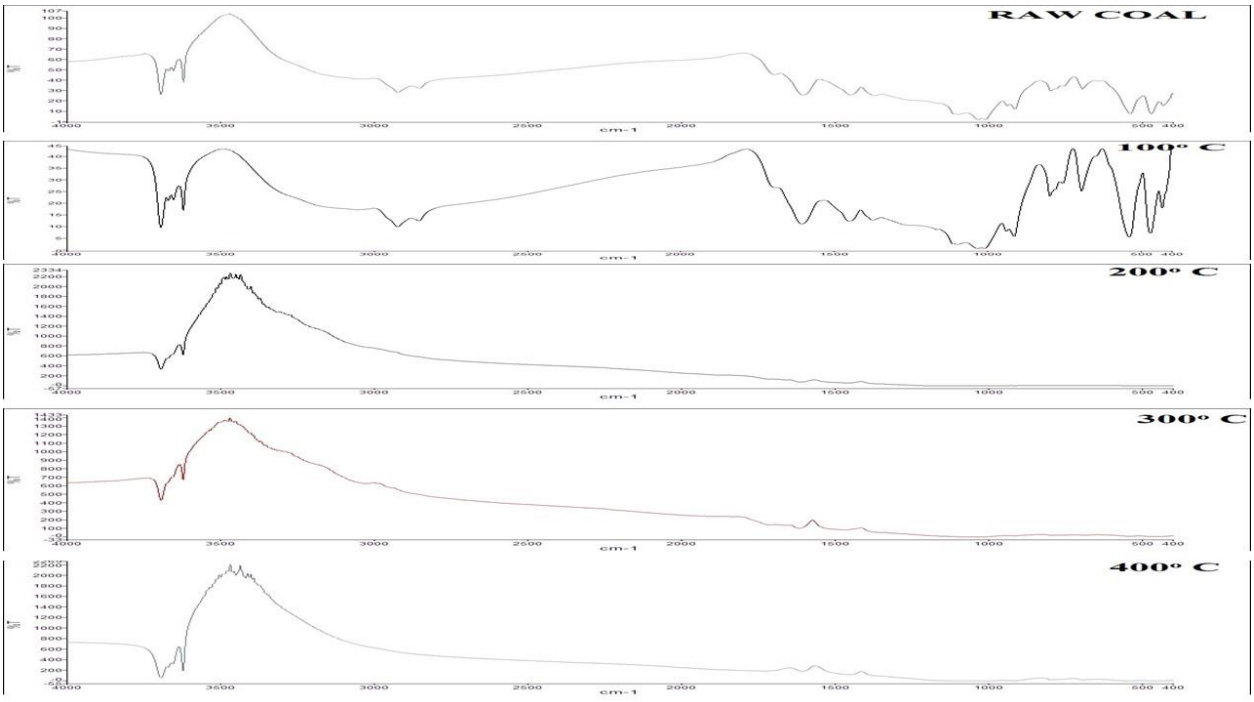

Fig A1.6 Comparison of FT-IR Spectrum at various temperatures, MCL – 06.

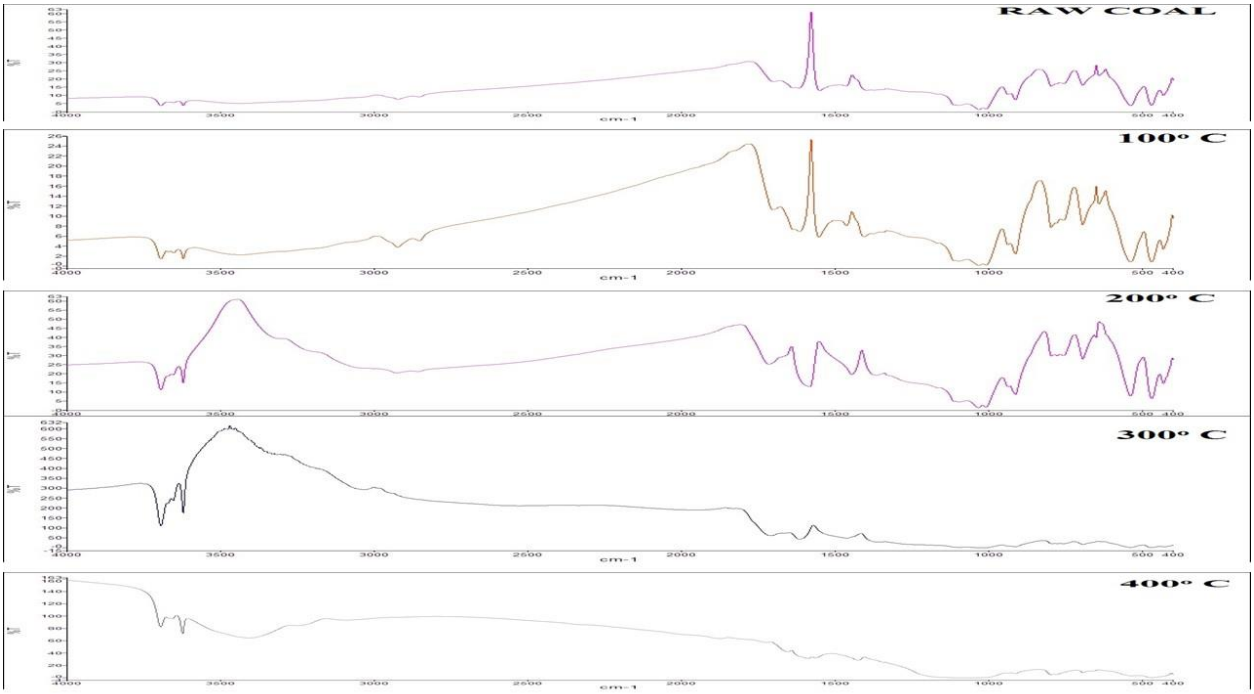

Fig A1.7 Comparison of FT-IR Spectrum at various temperatures, MCL – 07.

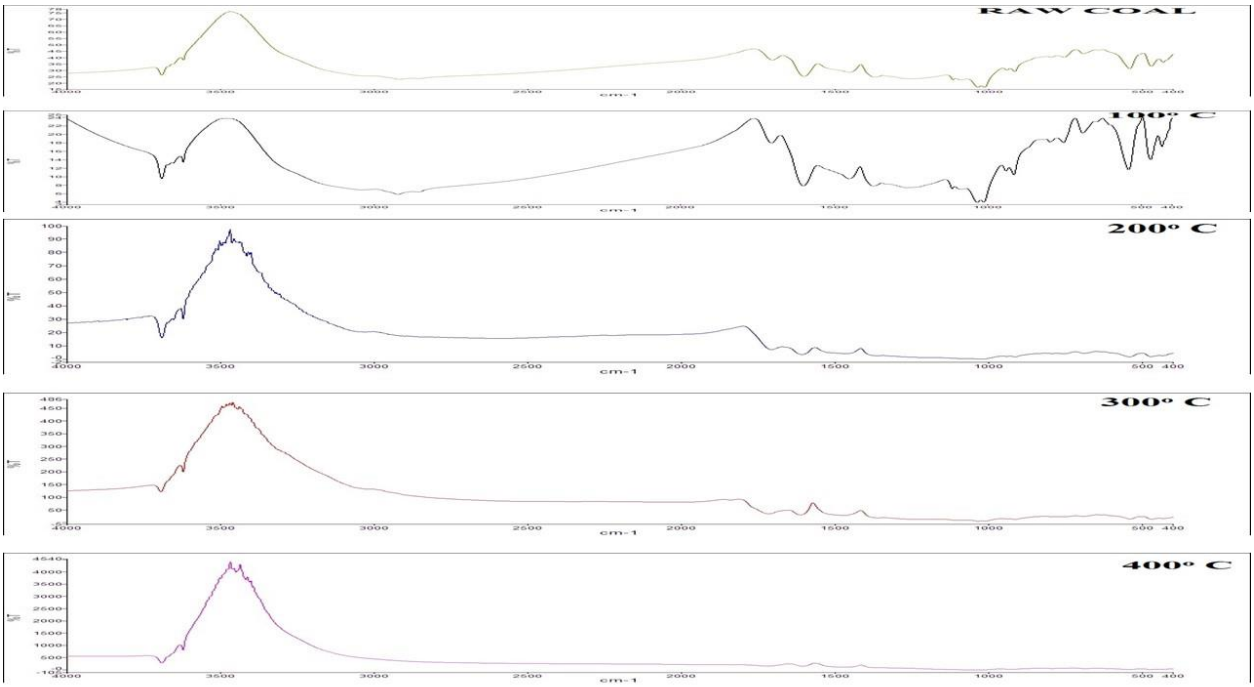

Fig A1.8 Comparison of FT-IR Spectrum at various temperatures, CCL - 01.

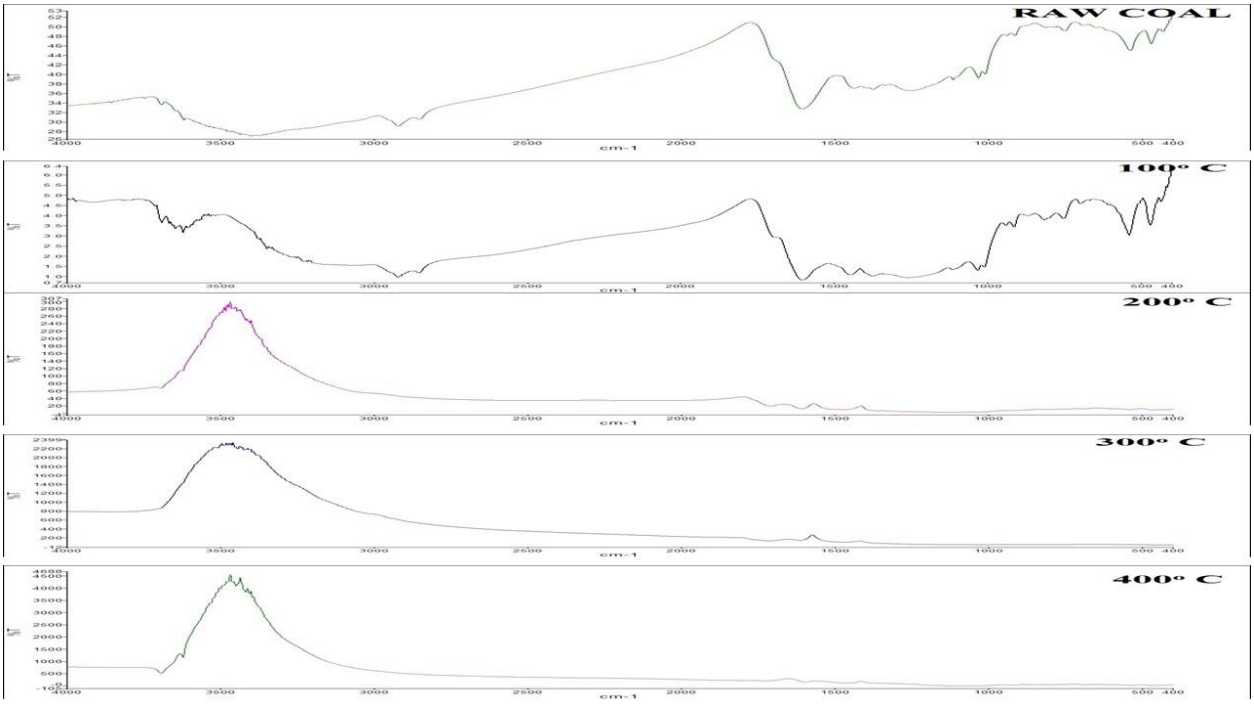

Fig A1.9 Comparison of FT-IR Spectrum at various temperatures, CCL – 02.

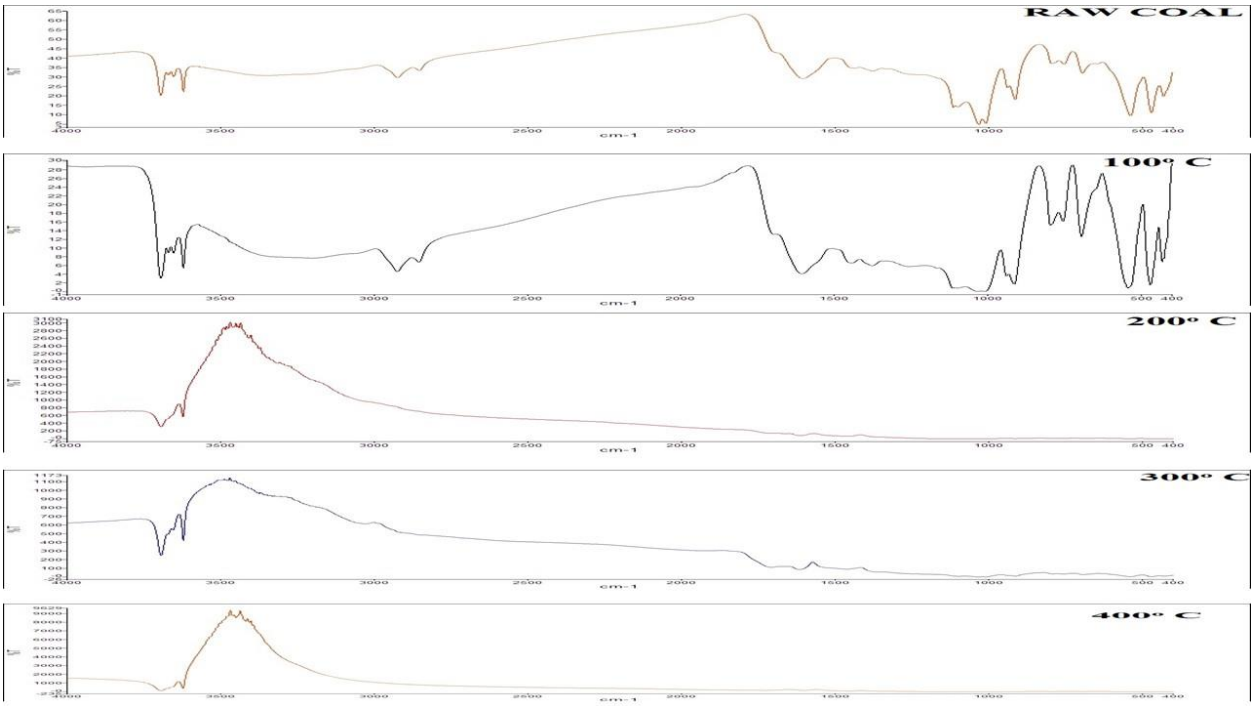

Fig A1.10 Comparison of FT-IR Spectrum at various temperatures, CCL – 03.

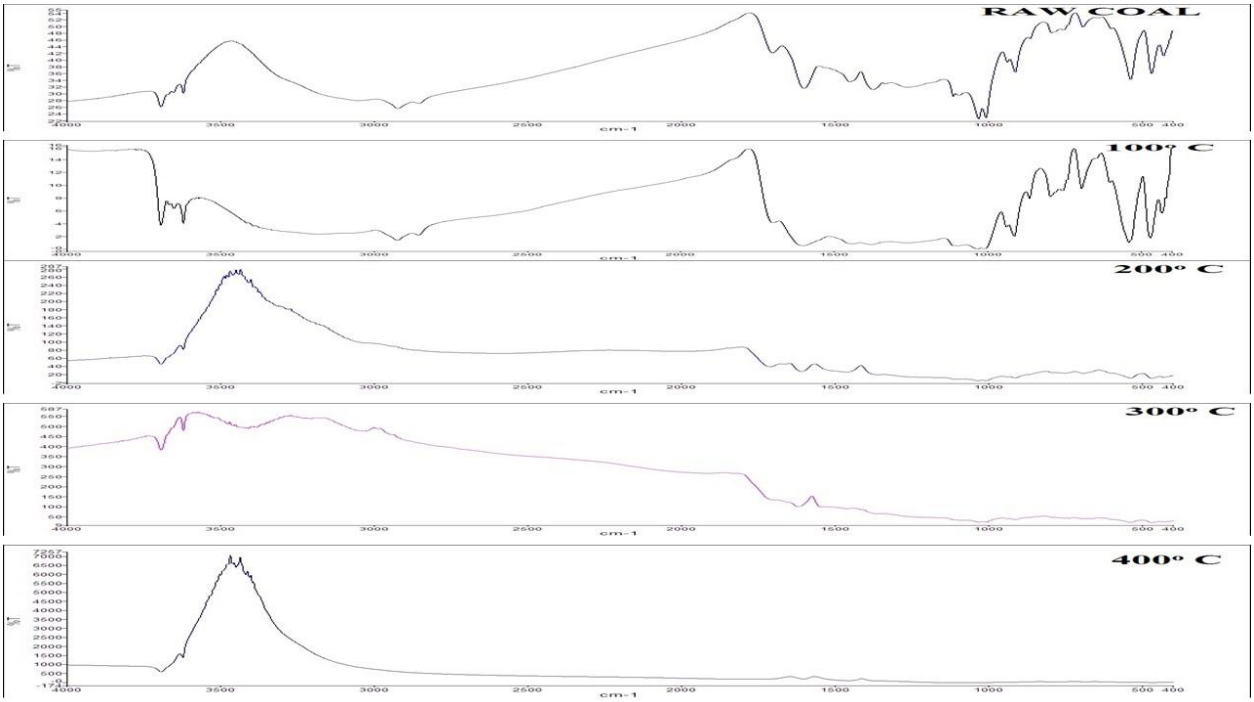

Fig A1.11 Comparison of FT-IR Spectrum at various temperatures, CCL – 04.

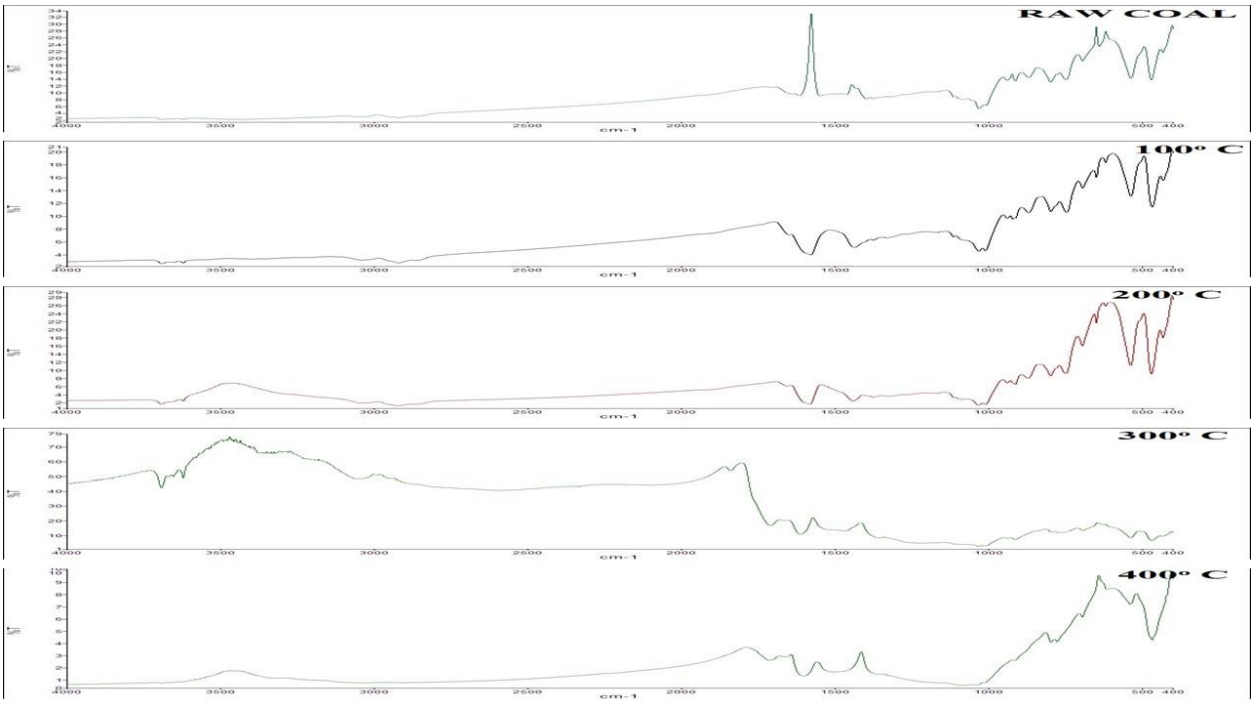

Fig A1.12 Comparison of FT-IR Spectrum at various temperatures, BCCL – 01.

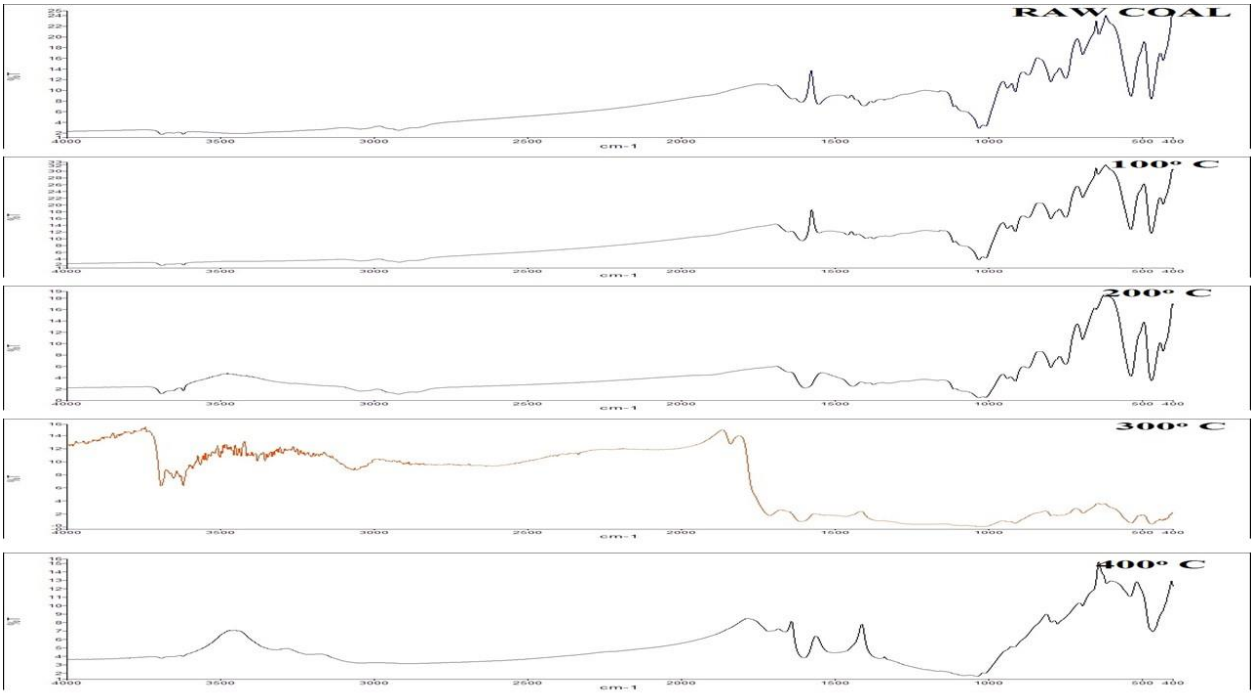

Fig A1.13 Comparison of FT-IR Spectrum at various temperatures, BCCL – 02.

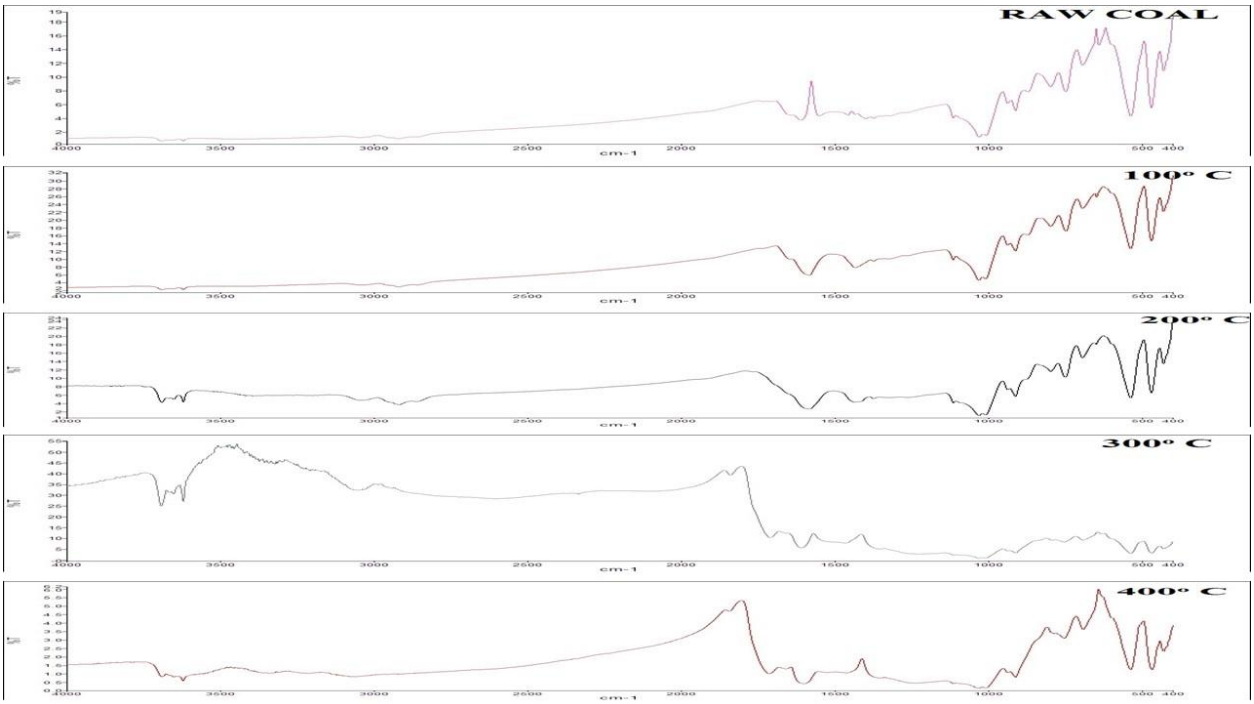

Fig A1.14 Comparison of FT-IR Spectrum at various temperatures, BCCL – 03.

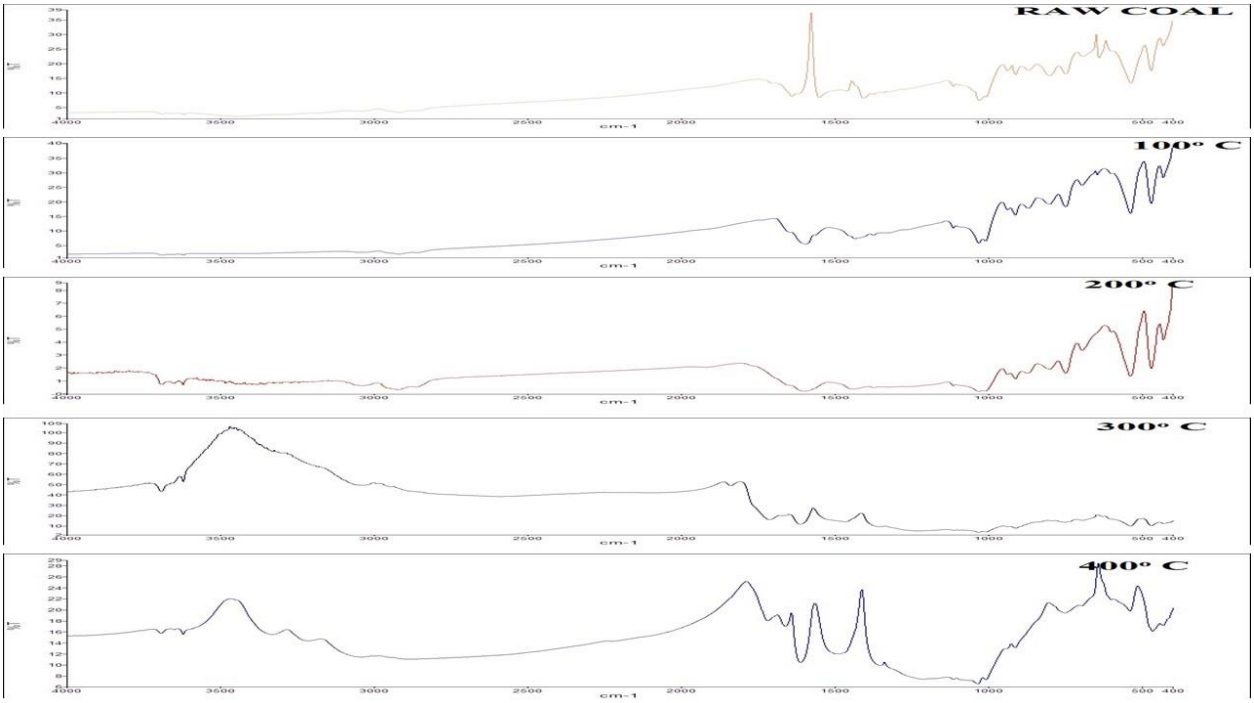

Fig A1.15 Comparison of FT-IR Spectrum at various temperatures, BCCL – 04.

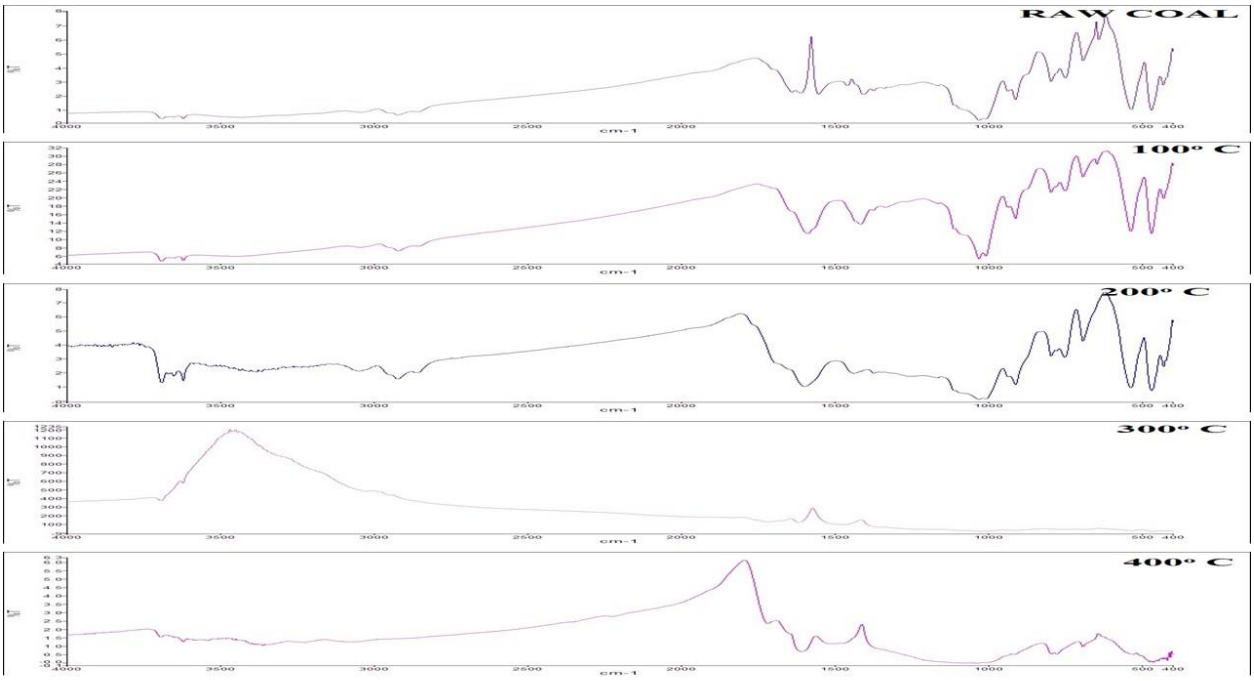

Fig A1.16 Comparison of FT-IR Spectrum at various temperatures, BCCL – 05.

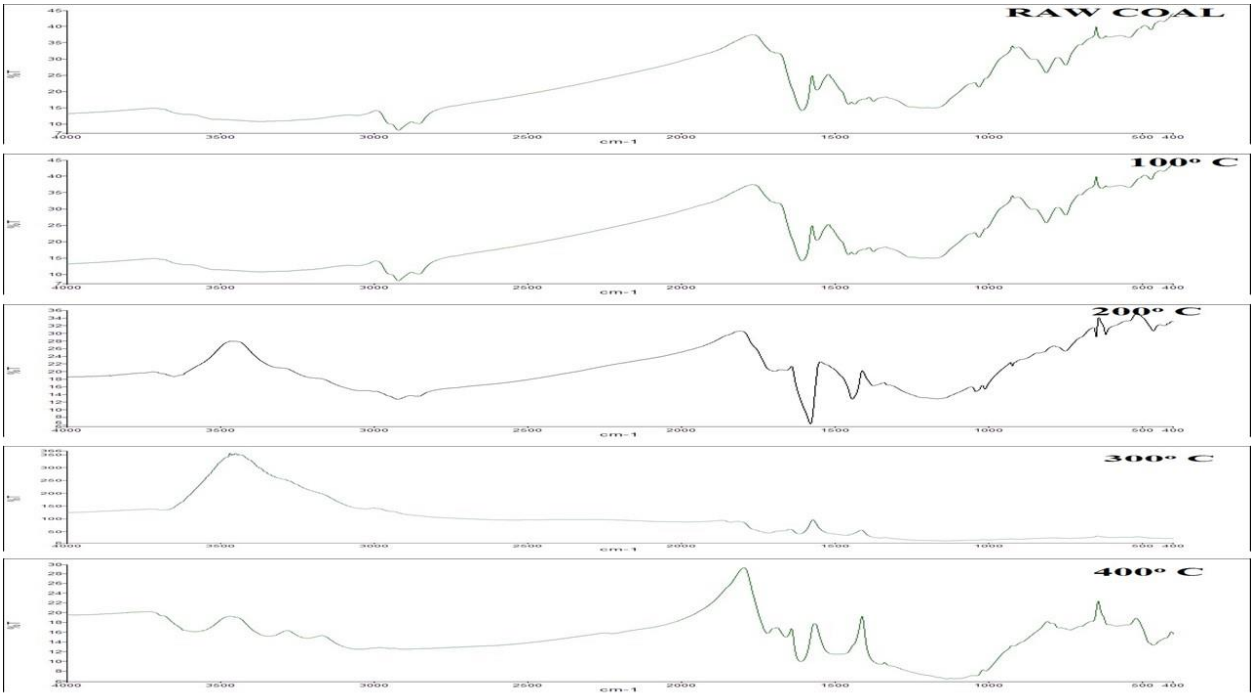

Fig A1.17 Comparison of FT-IR Spectrum at various temperatures, NEC – 01.

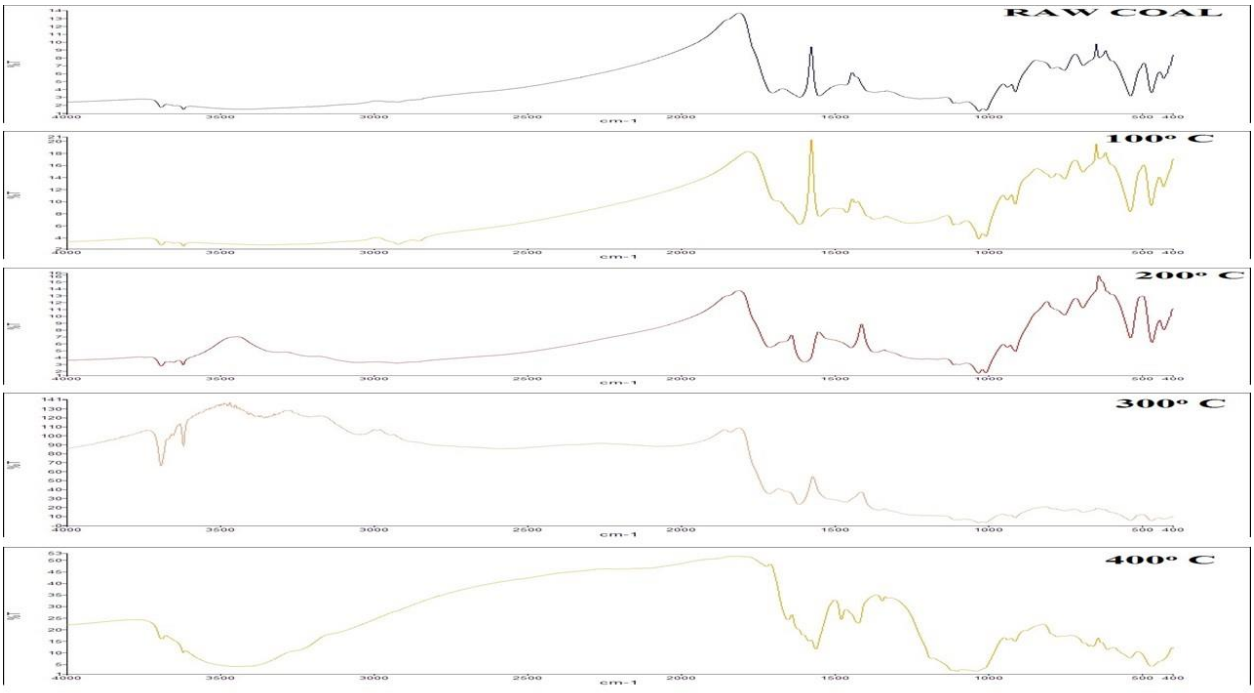

Fig A1.18 Comparison of FT-IR Spectrum at various temperatures, NEC – 02.

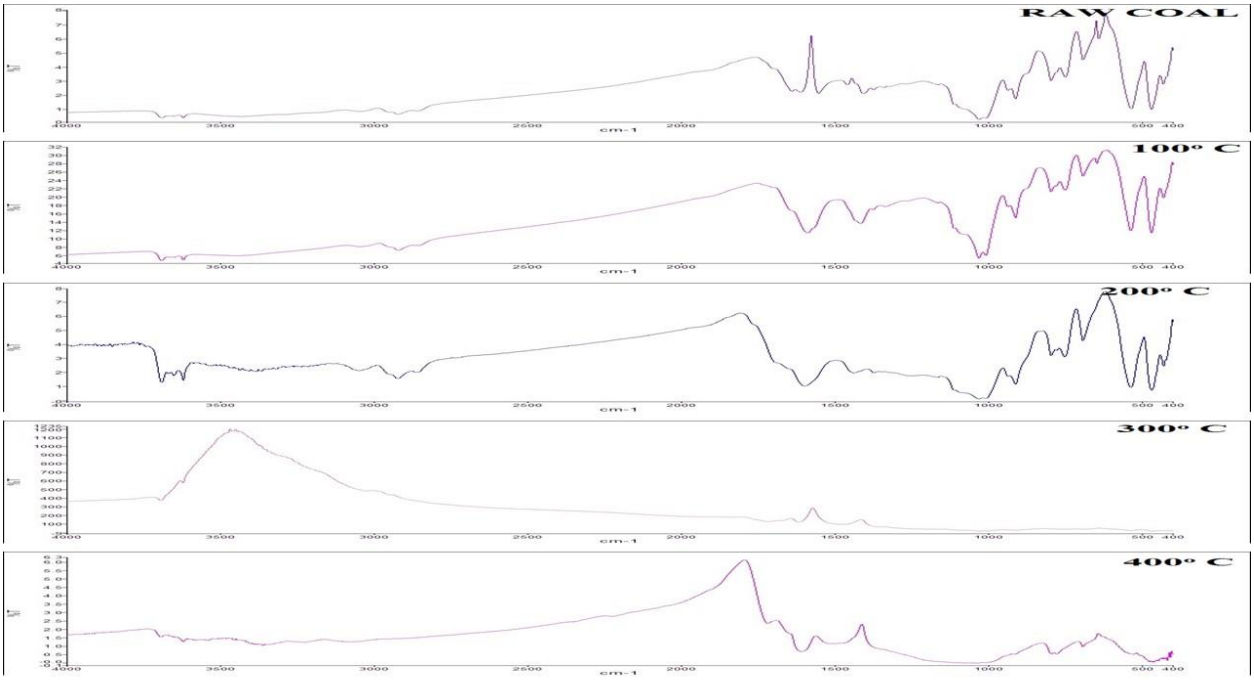

Fig A1.19 Comparison of FT-IR Spectrum at various temperatures, SCCL – 01.

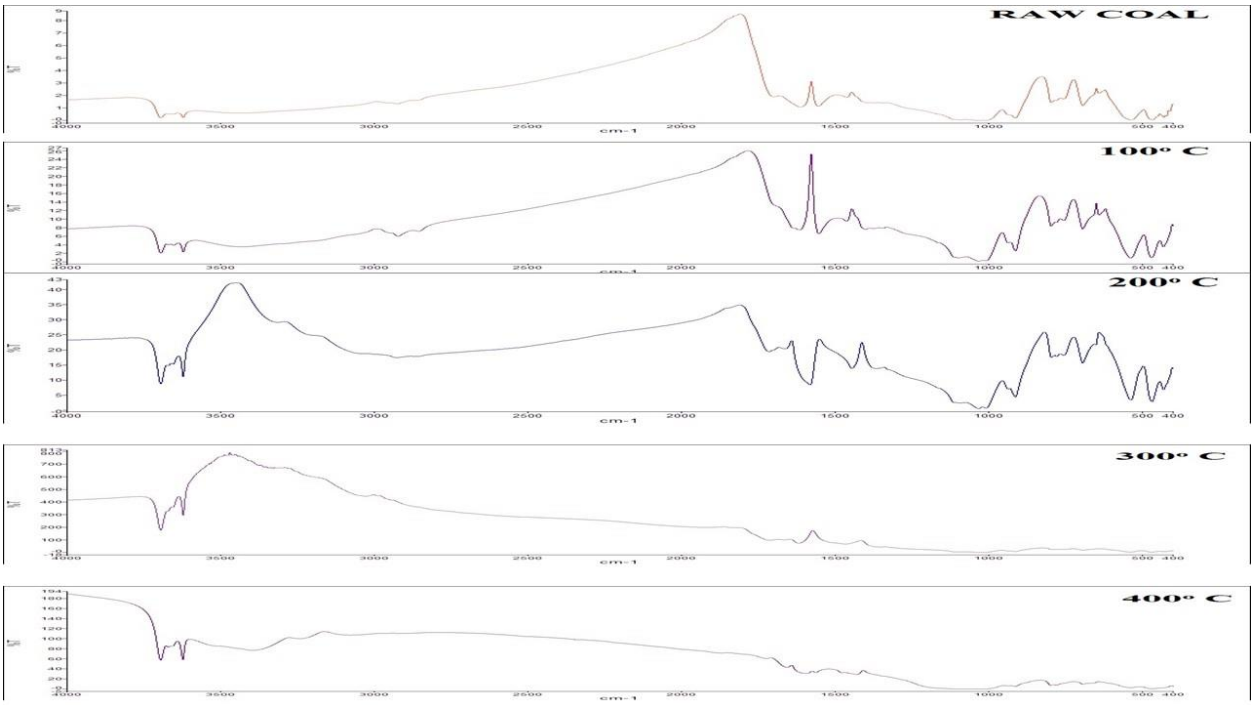

Fig A1.20 Comparison of FT-IR Spectrum at various temperatures, SECL – 01.